

Portable X-ray fluorescence for the detection of POP-BFRs in waste plastics

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Keywords: Waste Plastics; LPCL Screening; POP-BFRs; PBDEs; HBCDD; XRF
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Drage, PhD; Stuart Harrad, PhD; Harald Berresheim, PhD

Abstract: The purpose of this study was to establish the efficacy of portable X-Ray Fluorescence (XRF) instrumentation as a screening tool for a variety of end of life plastics which may contain excess amounts of brominated flame retardants (BFRs), in compliance with European Union (EU) and United Nations Environment Programme (UNEP) legislative limits (low POP concentration limits - LPCLs). 555 samples of waste plastics were collected from eight waste and recycling sites in Ireland, including waste electrical and electronic equipment (WEEE), textiles, polyurethane foams (PUFs), and expanded polystyrene foams. Samples were screened for bromine content, in situ using a Niton™ XL3T GOLDD XRF analyser, the results of which were statistically compared to mass spectrometry (MS)-based measurements of polybrominated diphenyl ethers (PBDEs), hexabromocyclododecane (HBCDD) and tetrabromobisphenol-A (TBBP-A) concentrations in the same samples.

Regression between XRF and MS for WEEE samples show that, despite an overall favourable trend, large deviations occur for a cluster of samples indicative of other bromine-based compounds in some samples; even compensating for false-positives due to background interference from electronic components, XRF tends to over-estimate MS-determined BFR concentrations in the 100 to 10,000 mg kg⁻¹ range. Substantial deviations were additionally found between results for PUFs, textiles and polystyrene samples, with the XRF over-estimating BFR concentrations by a factor of up to 1.9; this is likely due to matrix effects influencing XRF measurements. However, expanded (EPS) and extruded polystyrene (XPS) yielded much more reliable estimations of BFR-content due to a dominance of HBCDD in these materials.

XRF proved much more reliable as a "pass/fail" screening tool for LPCL compliance (including a prospective LPCL on Deca-BDE based on REACH). Using a conservative threshold of BFR content exceeding legislative limits (710 mg kg⁻¹ bromine attributed to penta-BDE), XRF mistakenly identifies only 6 % of samples (34/555) as exceeding legislative limits.

Response to Reviewers: Please see attached file "Response to Reviewers 2"

Dear Professor Covaci,

We would like to submit the following manuscript on behalf of the authors entitled “Portable X-Ray Fluorescence for the Detection of POP-BFRs in Waste Plastics” by Martin Sharkey, Mohamed Abou-Elwafa Abdallah, Daniel S. Drage, Stuart Harrad, and Harald Berresheim, to be considered as a *Full Research Paper* for Science of the Total Environment.

This manuscript focuses primarily on human activity within the anthrosphere: the current state of technology for the screening of flame retardant POPs, the requirements for screening as pertains to current EU legislation, and refinements to the protocols of said screening through a large-scale field study. The paper’s introduction establishes hazards within the biosphere associated with these flame retardant POPs as well as their ubiquity within the environment, hence their listing as POPs and establishment of concentration limits. The results and subsequent discussion then provide a statistical overview of the efficacy of the refined screening protocols in both qualitative and quantitative instances, then evaluating its practicable efficacy in waste and recycling systems. This paper will therefore have direct implications for environmental management and policy regarding recycling systems, helping to promote the circular economy and subsequent environmental remediation.

This is an original manuscript that has been approved by all named authors and is not currently being considered for publication elsewhere.

Thank you very much for your time, and we look forward to hearing from you with regards to the manuscript’s suitability for publications in Science of the Total Environment.

Sincerely,

Martin Sharkey

*PhD Candidate at Centre for Climate and Air Pollution Studies,
School of Physics, National University of Ireland Galway,
Republic of Ireland.*

Portable X-Ray Fluorescence for the Detection of POP-BFRs in Waste Plastics

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Author's agreement

We the undersigned declare that the manuscript entitled "**Portable X-Ray Fluorescence for the Detection of POP-BFRs in Waste Plastics**" is original, has not been full or partly published before, and is not currently being considered for publication elsewhere.

We confirm that the manuscript has been read and approved by all named authors and that there are no other persons who satisfied the criteria for authorship but are not listed. We further confirm that the order of authors listed in the manuscript has been approved by the undersigned.

We understand that the Corresponding Author is the sole contact for the editorial process. The corresponding author "**Martin Sharkey**" is responsible for communicating with the other authors about process, submissions of revisions, and final approval of proofs."

Signature of all authors:

Martin Sharkey



Mohamed Abou-Elwafa Abdallah



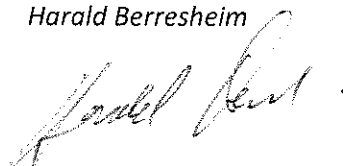
Daniel S. Drage



Stuart Harrad



Harald Berresheim



Reviewer #2:

However, Chapter 2.3: note that XRF spectroscopy is the main technique used in this paper and still technical details are missing ((K α , interferences etc etc):

The qualifier and quantifier lines, potential pitfalls like interferences and interference correction, this is really crucial and is still missing, please consider this to elaborate more on that !!

If the XRF software controls interferences than in must be addressed.

Thank you for outlining the details here which need to be expanded. A sentence has been included which states the qualifier and quantifier lines for the instrument:

“Quantification and qualification of bromine for the Niton XL3t model are achieved using the K α 1 line (11.9242 eV) and K α 2 line (11.8776 eV) respectively.”

Additional notes have also been included to expand on how and why certain interference corrections were carried out:

(i) removal of surface dust from samples – “For HIPS, ABS and insulation foam samples, the surface of the material was wiped with a clean non-fibrillating tissue prior to analysis, in order to remove sediment and dust which could interfere with the instrument’s primary x-rays or may contain traces of bromine.”;

(ii) thickness corrections for WEEE samples – “A thickness correction of 2 mm was additionally applied to the HIPS and ABS samples to help account for the finite thickness of the samples (per manufacturer guidelines); this reduces the risk of interference from substrate materials as the instrument internally estimates the density of an analyte based on Compton scattering of primary x-rays” (also outlined in section 3.2.2). Final paragraph of section 2.3 also includes a note on the additional test carried out to test the efficacy of thickness corrections, the results of which are noted in the Discussion section (lines 480-483);

(iii) thickness of samples for analysis – minimum thicknesses for analysis already outlined as that being required for full attenuation of primary x-rays, based on in-lab tests carried out by Thermo Fisher Scientific “Upholstery and other soft furnishings were manually folded, compressed to a thickness of approximately 3 cm (to achieve the thickness required for said materials for full attenuation of primary x-rays, per instrument manufacturer guidelines) and held in place by placing the instrument over the sample, in order to increase the density of the active analysis zone.”;

(iv) instrument mode of operation – “The instrument was operated in the “plastics” mode of operation, which optimises the instrument’s settings for interaction of x-rays with low density polymer materials and quantification of specific elements in their matrices.”

Reviewer #3:

The only text I would modify is that relating to scattered radiation being much less energetic than primary x-rays.

While the intensity of x-rays is reduced considerably, the energy is only modified by a few per cent.

Thank you for the correction; the sentence has been modified to reflect that the intensity of x-rays is reduced more significantly than the energy:

“As per Niton UK guidelines on the use of the device, secondary x-rays projected from the specimen deviate at angles around the device (mostly laterally) as well as at much lower intensities than primary x-rays, thus attenuating rapidly.”

1 Portable X-Ray Fluorescence for the Detection of POP-BFRs
2 in Waste Plastics

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12

Abstract

The purpose of this study was to establish the efficacy of portable x-ray fluorescence (XRF) instrumentation as a screening tool for a variety of end of life plastics which may contain excess amounts of brominated flame retardants (BFRs), in compliance with European Union (EU) and United Nations Environment Programme (UNEP) legislative limits (low POP concentration limits – LPCLs). 555 samples of waste plastics were collected from eight waste and recycling sites in Ireland, including waste electrical and electronic equipment (WEEE), textiles, polyurethane foams (PUFs), and expanded polystyrene foams. Samples were screened for bromine content, *in situ* using a Niton™ XL3T GOLDD XRF analyser, the results of which were statistically compared to mass spectrometry (MS)-based measurements of polybrominated diphenyl ethers (PBDEs), hexabromocyclododecane (HBCDD) and tetrabromobisphenol-A (TBBP-A) concentrations in the same samples.

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XRF proved much more reliable as a “pass/fail” screening tool for LPCL compliance (including a prospective LPCL on Deca-BDE based on REACH). Using a conservative threshold of BFR content exceeding legislative limits (710 mg kg⁻¹ bromine attributed to

38 penta-BDE), XRF mistakenly identifies only 6 % of samples (34/555) as exceeding
39 legislative limits.

40

41 **Keywords**

42 Waste Plastics; LPCL Screening; Quantification; PBDEs; HBCDD.

43

1. Introduction

Polybrominated diphenyl ethers (PBDEs) and hexabromocyclododecane (HBCDD) are two groups of brominated flame retardants (BFRs) which have been extensively applied to various commercial and consumer products to meet flammability standards. HBCDD has been used as a flame retardant additive in expanded (EPS) and extruded (XPS) polystyrene insulation foams as well as in high impact polystyrene (HIPS) for electrical housing and junction boxes, as well as a textile coating agent for furniture and furnishings (Marvin et al., 2011, UNEP, 2017b). Of the three commercial PBDE formulations, Penta-BDE is reportedly almost exclusively used in polyurethane foams (PUFs) for domestic, office and automotive applications, along with minor applications in printed circuit boards and microprocessors in electrical and electronic equipment (EEE) (UNEP, 2010). Octa-BDE has been applied to acrylonitrile butadiene styrene (ABS) and HIPS, largely used as casings for EEE (EC, 2011). Deca-BDE was commonly used in coating agents applied to the surfaces of textiles and upholstery as well as applied to HIPS for EEE as an additive compound (Weil and Levchik, 2009, IPCS, 1997). Over the last two decades however, concerns about their toxicity, persistence and ability to bioaccumulate has led to their listing as persistent organic Pollutants (POPs) under the Stockholm Convention. The commercial mixtures of Penta- and Octa-BDE were listed in 2009 (UNEP, 2009), whilst HBCDD was listed in 2013 (UNEP, 2013), and the Deca-BDE commercial mixture listed in 2017 (UNEP, 2017a). Another common legacy BFR, tetrabromobisphenol-A (TBBP-A), is also extensively used in as an additive in HIPS and ABS and also reactively added to printed circuit boards for EEE (Morf et al., 2003, IPCS, 1997). Though not currently under consideration for listing as a POP, TBBP-A has been recently classified as H410 (very toxic to aquatic species), and listed as a Class 2A carcinogen (Grosse et al., 2016, Malkoske et al., 2016). Additionally, waste articles

containing TBBP-A at concentrations in excess of 0.1 % is to be classified as “hazardous waste” (EU, 2017b).

In the light of growing environmental concern, measures are being adopted in order to prevent further environmental contamination from goods which were treated with POP-BFRs (UNEP, 2009, EC, 2004). One such measure is the modification of recycling systems to include screening procedures for goods suspected to contain high concentrations of POPs, including POP-BFRs. Low POP concentration limits (LPCLs) of 1000 mg kg⁻¹ have been established for each of the HBCDD, Penta-BDE and Octa-BDE commercial mixtures (EC, 2010, EC, 2016, EU, 2017a), in addition to a limit on Deca-BDE to come into force in 2019 (EU, 2017). However, a fast and cost-effective method of identifying products exceeding these limits has not yet been identified, with industry standards (such as conventional chromatographic-mass spectrometric techniques) being impractical for this purpose due to their high running costs and low throughput.

Recently the use of portable x-ray fluorescence (XRF) measurements of elemental Br has been suggested as a surrogate measure of POP-BFR concentrations. Several studies have been performed to investigate the efficacy of portable XRF for the measurements of BFRs in various plastic products, including EEE (Gallen et al., 2014, Aldrian et al., 2015, Guzzonato et al., 2016) and furniture fabrics, foams and textiles (Petreas et al., 2016). Whilst these studies have had varying degrees of success, they have all concluded that XRF-based measurements are not capable of accurately quantifying concentrations of specific BFRs as XRF measures elemental bromine only. However, Aldrian et al. (2015) and Petreas et al. (2016) suggested that the use of XRF may be an effective screening tool for bromine content in WEEE and furniture, as well as Schlummer et al. (2015) concluding effective screening potential of HBCDD with the inclusion of an extraction process to distinguish the Br species. Furthermore, Guzzonato et al. (2016) demonstrated that the accuracy of XRF measurements

of Br in ABS and HIPS may be improved by use of custom-made solid reference standards containing Deca-BDE, and concluded that use of XRF to screen waste electrical and electronic equipment (WEEE) for compliance with LPCLs was feasible. The largest recent study (Sindikú et al., 2015) includes XRF screening in their methodology using varying ranges of Br content, proving relatively successful in screening for BFR-content (with an instrumental precision of $\pm 20\%$) but does highlight limitations in discerning the species of bromine.

While the suitability of the XRF as a tool for predicting BFR concentrations has been evaluated previously, many of the studies hitherto have been on a relatively small scale (<50 samples). Moreover, the range of plastics previously studied is limited to a few types and applications or do not show in-depth comparisons of the accuracy and precision of XRF with respect to MS analysis. In light of the introduction of LPCLs and the substantial mass of waste polymers that will require screening for compliance with LPCLs (*e.g.* 42,628 tonnes of WEEE collected in Ireland in 2013 (EPA, 2016)), it is vital that a rapid screening method is developed to enable fast and reliable identification of waste items exceeding LPCLs. Therefore the aims of this study are to (i) examine the efficacy of portable XRF measurements as a predictor of BFR concentrations in a wide range of plastics in the waste stream; and (ii) to determine whether portable XRF can be used as a “pass/fail” screening tool for the interception of waste products exceeding LPCLs. These aims were achieved by a large scale sampling campaign of recyclable plastics at waste and recycling sites in Ireland. XRF measurements of bromine in a variety of waste articles (including WEEE plastics, domestic and end of life vehicle (ELV) soft furnishings (PUF and upholstery fabrics) and EPS/XPS insulation) were taken prior to quantitative analysis of selected BFRs via either GC/MS or LC-MS/MS. To our knowledge, this is the first assessment of XRF as a tool for monitoring compliance with LPCL legislation. Moreover, it represents the most

comprehensive assessment to date of the accuracy and suitability of hand-held XRF analysis for quantification of BFR levels in waste articles.

2. Materials and Methods

2.1 Materials

Chemical standards for native BDEs -28, -47, -77, -99, -100, -128, -153, -154, -183, -196, -197, -203, -209, native α -HBCDD, β -HBCDD, γ -HBCDD, $^{13}\text{C}_{12}$ -BDE-209, $^{13}\text{C}_{12}$ - α -HBCDD, $^{13}\text{C}_{12}$ - β -HBCDD, $^{13}\text{C}_{12}$ - γ -HBCDD, d_{18} - γ -HBCDD and $^{13}\text{C}_{12}$ -TBBP-A were purchased from Wellington Laboratories (Guelph, ON, Canada). PCB-129 was purchased from Accustandard (New Haven, CT, USA). All solvents (HPLC grade hexane, dichloromethane (DCM), iso-octane and methanol) and sulfuric acid (>95 %) were purchased from Fisher Scientific (Loughborough, UK).

2.2 Sample Collection and Field Measurement

Samples were obtained from eight waste and recycling sites in Ireland and their bromine concentrations measured *in situ* using a hand-held XRF device. Samples from a range of different waste categories were collected: HIPS and ABS hard plastic casings from WEEE; soft furnishings and textiles typical in both domestic and vehicular environments; and polystyrene foams from building insulation and packaging materials. Following collection and XRF analysis, destructive chemical analysis via GC-MS and LC-MS/MS was carried-out on small sub-samples taken from the same parent product, within the immediate vicinity of the area subjected to XRF analysis. This was performed to evaluate the accuracy with which

the XRF-determined bromine concentrations correlated with those of GC/MS or LC-MS/MS measurements of selected BFRs.

In total, matched Br and BFR measurements were obtained for 555 samples; *Table 1* provides an overview of the number of samples collected from each “waste type”. Following on-site use of the XRF instrument, small sections of the scanned areas ($\sim 1\text{-}2\text{ cm}^2$ for HIPS/ABS, upholstery and textiles, or $\sim 1\text{-}2\text{ cm}^3$ for polystyrene and PUF) were subsequently removed and individually stored in labelled polyethylene bags. These collected samples were then shipped to the University of Birmingham where concentrations of POP-BFRs and TBBP-A were determined.

2.3 XRF Analysis

Each measurement involved placing the XRF instrument directly on to the measurement surface, with the operator standing directly behind the instrument for the duration of the measurement. As per Niton UK guidelines on the use of the device, secondary x-rays projected from the specimen deviate at angles around the device (mostly laterally) as well as at much lower intensities than primary x-rays, thus attenuating rapidly. Using the secondary dose rates produced during plastics mode of operation, on plastic materials, and with varying substrates (air, concrete, wood, etc.), the maximum dose for the user (at the device’s trigger) was calculated for the sum of all measurements carried out and found to be well-below the annual dose for a category B radiation worker (*i.e. <20 mSv in any single year*).

Determination of total bromine content in the samples was carried out *in situ* using a Niton XLt3-900 GOLDD X-Ray Fluorescence Analyser. Calibration was performed by Niton UK using proprietary standards containing varying concentrations of relevant inorganic compounds in a polymer matrix. Quantification and qualification of bromine for the Niton

XL3t model are achieved using the K α_1 line (11.9242 eV) and K α_2 line (11.8776 eV) respectively. The instrument was operated in the “plastics” mode of operation, which optimises the instrument’s settings for interaction of x-rays with low density polymer materials and quantification of specific elements in their matrices. Standard analyses using the XRF instrument in this mode gives a 95 % confidence interval ($CI = \pm 2\sigma$) with each measurement taken. The duration of analysis ranged from 30 to 105 seconds with longer iterations required to improve instrumental uncertainty in samples with high bromine content and for samples comprising of low density materials (Zawisza, 2012).

For HIPS, ABS and insulation foam samples, the surface of the material was wiped with a clean non-fibrillating tissue prior to analysis, in order to remove sediment and dust which could interfere with the instrument’s primary x-rays or may contain traces of bromine. A thickness correction of 2 mm was additionally applied to the HIPS and ABS samples to help account for the finite thickness of the samples (per manufacturer guidelines); this reduces the risk of interference from substrate materials as the instrument internally estimates the density of an analyte based on Compton scattering of primary x-rays. The instrument window was then placed flat against the sample surface and a measurement of bromine content carried out (with a minimum thickness of 10 cm for insulation samples and as presented at approximately 2 mm for HIPS and ABS samples). Upholstery and other soft furnishings were manually folded, compressed to a thickness of approximately 3 cm (to achieve the thickness required for said materials for full attenuation of primary x-rays, per instrument manufacturer guidelines) and held in place by placing the instrument over the sample, in order to increase the density of the active analysis zone. Three repeat measurements were carried out on each sample, several centimetres apart from each scanning point and at varying orientations. These repeat measurements were required to be carried out on the same plastic panel/area and under

the same experimental conditions in order to detect instances of heterogeneous distribution of BFRs within the body of sample.

Additional XRF measurements of bromine concentrations on available sub-samples of WEEE HIPS and ABS samples (i.e. those aliquots removed for BFR determination) were carried out in a controlled laboratory setting. These measurements were made in order to determine the instances where bromine detected during field measurements were due to background interference, being attributed to the presence of bromine in underlying electronic components rather than from the polymeric casing itself.

2.4 Extraction and Clean-Up

For quantitative analysis of BFRs, samples were extracted and cleaned according to methods previously described (Abdallah et al., 2017). Briefly, aliquots of samples (20-100 mg) were cut with a retractable blade and weighed directly into a 15 mL glass centrifuge tube and spiked with 20 ng of BDEs -77 and -128, $^{13}\text{C}_{12}$ - α -, β -, and γ -HBCDD, $^{13}\text{C}_{12}$ -TBBP-A, and 40 ng $^{13}\text{C}_{12}$ -BDE-209 as internal standards. Approximately 3 mL of dichloromethane (DCM) was added to the aliquot and vortexed for 2 minutes, followed by 30 minutes sonication. The extraction process was repeated three times with the combined extracts collected in a separate glass centrifuge tube. Crude extracts were concentrated under a gentle stream of N_2 to near-dryness and reconstituted in 2 mL hexane. Extracts were washed with >95 % sulfuric acid and supernatant organic layer was collected and concentrated to near-dryness under a gentle N_2 stream. Samples were reconstituted in 200 μL of iso-octane containing 0.2 ng μL^{-1} PCB-129 as a recovery standard. After determination of PBDEs via GC-MS, extracts were reconstituted in methanol containing 0.2 ng μL^{-1} d_{18} - γ -HBCDD for determination of HBCDDs and TBBP-A via LC-MS/MS analysis.

212

213 **2.5 Mass Spectrometric Analysis**

214 Quantitative analysis of PBDEs was performed in a single injection on a ThermoFisher Trace
215 1310 gas chromatograph coupled to a ThermoFisher ISQ mass spectrometer (MS). The MS
216 was operated in electron ionisation mode using selective ion monitoring (SIM). One μL of
217 the purified extract was injected for analysis using a programmable temperature vapouriser
218 (PTV) onto a Restek Rxi-5Sil MS column (15m x 0.25 mm x 0.25 μm film thickness).
219 Helium was used as the carrier gas at a flow rate of 1.5 mL min^{-1} . Full GC/MS parameters
220 have been reported previously (Abdallah et al., 2017).

221 HBCDDs were measured using a Shimadzu LC-20AB Prominence binary pump liquid
222 chromatograph equipped with a Sil-20A auto sampler and a DGU-20A3 vacuum degasser
223 coupled to an AB Sciex API 2000 triple quadrupole MS. Chromatographic separation was
224 achieved using Agilent Pursuit XRS3 C18 column (150 mm x 2 mm, I.D., 3 μm particle size)
225 and a mobile phase of (a) 1:1 methanol/water and (b) methanol at a flow rate of $180 \mu\text{L min}^{-1}$.
226 Molecular ionisation was achieved using an electrospray ionisation (ESI) source operated in
227 negative ion mode. The MS/MS was operated in the multiple reaction monitoring (MRM)
228 mode. The MRMs transitions monitored were on m/z $640.6 \rightarrow 79$, m/z $652.4 \rightarrow 79$ and m/z
229 $657.7 \rightarrow 79$ for the native and the $^{13}\text{C}_{12}$ -labelled HBCDD diastereomers respectively and
230 $540.8 \rightarrow 79$, m/z $552.8 \rightarrow 79$ were used to monitor native and $^{13}\text{C}_{12}$ -labelled TBBP-A. Full
231 LC-MS/MS parameters have been reported previously (Abdallah et al., 2008).

232

233 **2.6 Quality Assurance/Quality Control**

234 For BFR analysis, a reagent blank consisting of 100 mg of anhydrous sodium sulfate was
235 analysed with every batch of 11 samples. "Control" samples were created using plastics and

textiles that contain no BFRs and were also analysed throughout the study; three Controls were assessed for each matrix. None of the target compounds were found above the limits of detection in the blanks. Therefore results were not corrected for blank residues and method limits of detection (LOD) and quantification (LOQ) were estimated based on a signal to noise ratio (S/N) of 3:1 and 10:1 respectively.

Method accuracy and precision was assessed via repeated analysis of certified reference materials (CRMs) ERM-EC591 (polypropylene), ERM-EC590 (polyethylene) in addition to textiles (polyester fabrics), extruded polystyrene and expanded polystyrene that have been previously measured by this laboratory and another. All values were found to be close to certified or indicative levels, with a relative standard deviation of <15 % (Abdallah et al., 2017).

2.7 Exclusion Criteria for Regression Analysis

The regression analysis comprised a comparison between XRF-determined bromine, and the equivalent bromine concentrations attributed to quantified BFRs (see supporting information, S2). However, the accuracy of the XRF instrument must be taken into consideration for the regression between its results of bromine concentrations and those from the mass spectrometric analyses. The XRF instrument displays as a 95 % confidence interval or ± 2 standard deviations ($\pm 2\sigma$) for each analysis carried out; although this value can be altered, it provides a sufficiently concise confidence interval to establish the stability of analyses.

During the analysis of EPS and XPS foam samples using the XRF device, a $\pm 2\sigma$ interval as high as 16 mg kg⁻¹ bromine occurred with a “null” reading (i.e. the value determined by the XRF instrument was 0 ± 16 mg kg⁻¹), thus a conservative 20 mg kg⁻¹ value was chosen as the XRF analyser’s limit of detection (LOD_X). For the remaining polymeric materials – PUF,

HIPS, ABS, upholstery, textiles – a LOD_x of 10 mg kg⁻¹ was chosen using the same criteria as established for XPS and EPS samples (with a max $\pm 2\sigma$ interval of 8 mg kg⁻¹ for these sample groups). Therefore, in instances where each of the triplicate XRF measurements conducted on each sample fell below the LOD_x, that sample was not considered for the regression analysis. If, however, one of the triplicate measurements was above the LOD_x (and even if the average was below), the sample was included, in consideration of possible non-uniform BFR distribution throughout the body of the sample.

3. Results

3.1 Total Bromine Concentrations Determined by XRF Analyses

Table 1 shows a summary of the bromine concentrations quantified using the XRF during *in situ* analyses. Highest bromine concentrations were detected in the WEEE waste category at 110,000 mg kg⁻¹ and 150,000 mg kg⁻¹ in IT & Telecoms and Display samples respectively. Very high concentrations (exceeding 10,000 mg kg⁻¹) were also detected in the Furniture Upholstery, ELV Upholstery, and ELV (other) sample groups. The Fridge/Freezer, Curtain, C&D XPS, Mattress Foam and Mattress Upholstery sample groups showed very low maximum Br concentrations (< 1,000 mg kg⁻¹) along with low median and mean values. This indicates that these sample groups underwent low levels of treatment with bromine-containing compounds, and/or experienced transfer of bromine-containing compounds while in use or during storage for recycling/transfer (Rauert et al., 2014). The remaining sample groups showed maximum bromine content between 1,000 and 10,000 mg kg⁻¹ which, along with the aforementioned groups with concentrations in samples reaching roughly 150,000 mg kg⁻¹ Br, demonstrates potential from some articles in these groups to exceed LPCLs. However, as is evidenced by the low median concentrations for the sample groups relative to

the maximum values, samples with excessively high concentrations of bromine make up a minority of each remaining sample group. This indicates a relatively low proportion of waste articles potentially treated with POP-BFRs in these sample groups (with the possible exception of Display, Furniture Foam, Furniture Upholstery, and Vehicle Foam samples groups).

We have additionally observed so-called “false-positives” in different waste categories. A “false positive” corresponds to a situation where the XRF measurement of Br indicates the LPCL for a POP-BFR to be exceeded, but the POP-BFR concentration is below the LPCL. By comparison, a “false negative” would occur where the POP-BFR concentration is above the LPCL, but this is not indicated by the XRF measurement of Br. These occurrences will be reported by waste category in the following sections.

3.2 XRF – MS Total Bromine Measurement Comparison

Concentrations of BFRs in the samples included in this study have been previously reported by Drage et al. (2018). For comparison with XRF measurements they have been briefly outlined in *Table 1*. Additionally, following MS-analysis of the collected samples, some sample groups including the Mattress, Curtain, Carpet, ELV (other), Fridge/Freezer, and ELV (other) sample groups showed either no excessive concentrations of BFRs or very few samples with excess concentrations. These groups were therefore considered unsuitable to act as comparative metrics for regressions between MS and XRF analyses.

3.2.1 – WEEE Hard Plastics

In addition to the 65 WEEE samples excluded based on $Br < LOD_x$ (*Section 2.7*), a further 15 samples were omitted from the regression analysis due to laboratory confirmation of a background interference during *in situ* measurements of the samples (*Section 2.3*). *Table 2*

shows the results obtained for these 15 samples, comparing the average of the on-site triplicate XRF measurements to lab-based duplicate XRF measurements, the latter more accurately equating to the actual concentrations of bromine in the samples.

Application of this additional exclusion criterion yielded a final data set of 70 ABS/HIPS samples remaining for regression analysis, the result of which is shown in *Figure 1*. The linear regression coefficient (slope, m) is 0.98 and the coefficient of determination (R^2) is 0.614. However, a notable cluster of samples ($n = 10$) show much higher concentrations of bromine as determined by XRF analysis compared to the concentrations determined by GC/MS / LC-MS/MS analysis (defined here as “true” Br content). *Figure 2 (a)* is a Bland-Altman plot showing the variation in the Br content determined via XRF analysis as a percentage of true Br content $[((\text{XRF-MS})/\text{MS}) \times 100]$, where it can be seen that these outliers show at least a 4.9-fold overestimation of “true” Br content (z-test, $p < 0.001$) compared to a maximum of 2.4-fold overestimation in the remainder. It is likely therefore that these samples contained bromine in BFR-type chemicals other than those analysed for by the MS methods used herein, such as BTBPE, tetrabromophthalic acid, and DPDPE (Al-Omran and Harrad, 2016, Petty et al., 2016, IPCS, 1997).

Figure 2 (b) highlights large variations still exist between Br concentrations obtained for the same samples via the two measurement techniques. Samples with similar concentrations of BFRs show varying deviations between the techniques such that even employment of a correction factor would have limited success in improving the regression, across all concentrations shown herein. For example, samples with total Br concentrations ranging between 100 and 1,000 mg kg^{-1} show deviations from -3 % to +250 % between the analysis techniques for approximately 60 % of all WEEE samples therein. These variations may in part be due to the presence of NBFRs alongside TBBP-A, HBCDD and PBDEs, reflecting the

XRF instrument's inability to specify the precise chemical form of bromine present in samples.

3.2.2 – Furniture and Vehicle Foam

The XRF and MS derived concentrations of Br in 43 PUF samples are compared (*Figure 3*) showing a slope of 1.70 and a R^2 value of 0.98. The high regression coefficient for these samples is likely the result of interferences with primary and secondary x-rays in the high thickness and low density of the PUF samples examined. Internal XRF approximations of the sample's density using Compton scattering can be heavily influenced due to the presence of air pockets in the samples, leading to a significant bias in the accurate quantification of elemental bromine (and other elements) (Zawisza, 2012). However, assuming these biases are relatively consistent throughout different PUF samples, measured results can be subsequently multiplied by a correction factor derived from the inverted slope of linear regression to correct this bias.

Although this correction factor ($\mu_{\text{puf}} = 1.70^{-1} = 0.59$) can improve the accuracy of the XRF-measurements, its precision in the analysis of PUF samples remains unreliable, with relative standard deviation (RSD) for individual measurements ranging from 1 % to 172 % ($\text{RSD}_{\text{avg}} = 39 \%$). In addition, repeated XRF analyses of PUF samples on a dedicated test stand in a controlled laboratory setting showed high variability in Br content depending on the orientation of the sample and the surface facing the analyser window. It was observed upon repeated laboratory measurements of eight furniture foam samples whose XRF results deviated by >250 % from the corresponding MS-concentrations, that five of the samples had shown substantial differences (z-test, $p < 0.001$) in the detected concentration of bromine on surfaces which were cut away from the body of the PUF item compared to the surface adjacent to the upholstery (*S1 (a), S4*). This – akin to previous observations of BFR migration

from fabric to dust via direct contact (Rauert et al., 2016) is consistent with migration of BFRs from overlying upholstery fabric into underlying PUF, resulting in higher concentrations of BFRs in PUF near contact surfaces and spatially declining concentrations deeper within the material.

3.2.3 – Furniture and Vehicle Upholstery

For the regression of the 66 upholstery samples included a slope of 1.38 and a R^2 of 0.86 were determined (*S5 (a)*), indicating a strong correlation between the analytical techniques. Similar to the PUF samples, the upholstery samples also appear to require a correction factor ($\mu_{\text{upholstery}} = 1.38^{-1} = 0.72$) in order to account for the relatively low density of the material and the resultant matrix effects. However, a Bland-Altman plot similar to *Figure 2 (a)* demonstrated the XRF's overestimation of bromine concentrations by up to 180 % for concentrations exceeding 100 mg kg^{-1} and several thousand percent for lower concentrations. This phenomenon may simply be more obscured at larger concentrations due to the magnitude of concentrations involved and also possibly due to a “screening-effect” within the matrix of the material during XRF analysis, whereby multiple bromine atoms are in a linear formation with respect to the analyser resulting in only the first and none of the subsequent bromine atoms being detected (Zawisza, 2012).

The relative homogeneity of repeated XRF measurements and the high discrepancies between Br concentrations obtained via the two measurement techniques revealed in the Bland-Altman plot (*S1 (b)*), are – as for PUF materials – likely attributable to the presence of BFRs not measured in this study or, in the case of some ELV samples containing green upholstery, the use of green pigment containing bromine. In similar fashion to WEEE samples (*Section 3.2.1*), only 25 % of samples yielded Br concentrations derived by XRF that agreed within ± 25 % of those obtained via MS (following application of the correction factor). However,

given the high treatment concentrations with HBCDD and Deca-BDE, the XRF could still be successfully applied to the screening of upholstery for excess POP-BFRs as false-positives (instances where XRF analysis indicates exceedance of an LPCL where none actually occurred) at such elevated bromine concentrations were rare in this study.

3.2.4 –Insulation Foams - Expanded Polystyrene (EPS)

Of the 47 original EPS samples, 17 were excluded from the analysis due to determination of Br concentrations below LOD_x. Br concentrations obtained for the remaining samples via XRF and MS underwent regression analysis (*Figure 4*) showing a linear slope of 1.20 and R² of 0.98. The XRF measurements again appear to require a calibration factor in order to correct the regression for offsets caused by matrix effects. Implementing this, XRF measurements of 16 out of 30 samples correlate to within 25 % of MS results with 12 of these 16 (for which Br >1000 mg kg⁻¹) agreeing to within 10 % of MS-determined bromine content.

Despite this favourable agreement for samples containing higher Br concentrations (i.e. >1000 mg kg⁻¹) analysis of the data using a Bland-Altman plot (*SI (c)*) reveal potentially significant outliers in this sample group most notably in the 0-10 mg kg⁻¹ Br concentration range (z-test, p < 0.05), as determined by MS analysis, despite exclusion of samples <LOD_x. Additionally, the relative standard deviations (RSDs) of the triplicate XRF measurements indicate that the samples showing poor agreement between XRF and MS have large RSDs (>25 %) between the individual XRF measurements, the largest RSDs (173 % each) being attributed to the significant outliers highlighted in *SI (c)*. Selection criteria for more accurate categorisation of Br concentrations can potentially be established from these observations; specifically, omission of samples with 0-10 mg kg⁻¹ Br-content (from MS analysis) and those

with RSDs over 25 % (from triplicate XRF analysis, results in over 80 % of samples being categorised as accurate to within 10 % of the true HBCDD concentration.

One noteworthy EPS sample showed a much larger discrepancy between XRF-determined bromine (average bromine = 3354 mg kg⁻¹; RSD = 12 %) and LC-MS/MS (total bromine = 1030 mg kg⁻¹) analyses. Repeat XRF measurements of the same sample in-lab yielded an average for four measurements of 4275 mg kg⁻¹ bromine with a RSD of 19 % – the higher RSD being attributable to the small sample size relative to the XRF measurement window, such that primary x-rays are not interacting with the target sample. Such a variation between XRF-determined- and LC-MS/MS-determined bromine did not occur in any other samples within this group, potentially indicating another bromine-based compound in this particular sample, such as tribromoallylether or PolyFR (Schlummer et al., 2015, IPCS, 1997).

3.2.5 –Insulation Foams - Extruded Polystyrene (XPS)

The linear regression for the 20 XPS samples for which XRF- and MS-derived Br measurements were compared (*S5 (b)*) shows a linear slope of 1.93 with a R² of 0.97. This sample group shows the largest deviation from a unity regression. Following correction, a Bland-Altman plot (*SI (d)*) shows an even distribution for samples for containing >200 mg kg⁻¹ bromine. However, the variation between the two Br metrics at concentrations up to 200 mg kg⁻¹ remains high (±100 %).

This sampling, however, contained only a few with excessive concentrations of BFRs, and too few overall for a more definitive linear regression. Relatively few samples have been treated with BFRs and generally at much lower concentrations and other waste categories based on this sampling. However, a more statistically significant sample size may reveal as yet unseen nuances to this plastic.

4. Discussion

4.1 Utility of XRF Instrumentation as a Pass/Fail Screening Tool for LPCL Compliance

In the context of portable XRF's potential use as a tool for testing compliance with POP-BFR LPCL values, the incidence of "false positives" and "false negatives" is crucial. A "false positive" is defined here as a specific source misclassification scenario, i.e. a situation where the XRF measurement of Br indicates the LPCL for a POP-BFR to be exceeded, but the POP-BFR concentration is below the LPCL. By comparison, a "false negative" occurs where the POP-BFR concentration is above the LPCL, but this is not indicated by the XRF measurement of Br (*Section 3*). For the purposes of discussion here, we have assumed a conservative Br LPCL value based on the Br detected being due to penta-BDE. Thus, any sample exceeding 710 mg Br/kg is assumed here to exceed the POP-BFR LPCL of 1,000 mg POP-BFR/kg (including 1000 mg kg⁻¹ limit for Deca-BDE established by REACH).

Of the 555 items we tested, there were 34 false positives and no false negatives when the current LPCLs for POP-BFRs are considered: 26 occurred in WEEE items (1 large household appliance, 12 display items, 6 small domestic appliances, and 7 IT items); the remainder, in 2 vehicle fabric samples, 1 vehicle foam sample, 1 carpet sample, 1 mattress foam sample, 1 furniture upholstery sample, and 2 furniture foam samples. These resulted from concentrations >1,000 mg kg⁻¹ of either TBBP-A alone (n=15), as yet unidentified bromine-containing compounds (n=11), and in 8 instances enhancement of measured BFR concentrations. However, 5 of the 11 samples with unidentified compounds are attributable to false-positives due to background interference (*Section 3.2.1*) which therefore reduces the number of false-positives to 29 of 555. Translating these incidences into percentages, our data show that use of portable XRF to monitor compliance with current LPCLs for PBDEs and HBCDD would mean that 5.2 % of articles from the waste categories studied would be

incorrectly identified as requiring special treatment. This compares to 47 (8.5 %) of articles identified as genuinely exceeding current LPCLs and REACH limits.

The implications of such false positives are essentially that a small additional percentage of articles will not be available for recycling and that there will be an additional unnecessary economic cost incurred when such articles are subjected to special treatment. Balanced against these issues, it may be argued that as the cause of the false positives are likely to be either known or unidentified BFRs not targeted in our study, which may themselves become subject to future legislative restriction; false positives can potentially be viewed as an acceptable limitation of the use of XRF as a screening tool for LPCL compliance. By comparison, false negatives would exert a more detrimental impact as they would allow regulated POP-BFRs to remain in circulation. However, the absence of false negatives in our study, suggests that use of hand-held XRF will only very rarely – if ever - fail to identify articles that exceed LPCL values.

Our data on false positives indicate that portable XRF could be a viable tool for testing compliance with LPCLs for EPS/XPS, as well as ELV waste and waste soft furnishings, while further underlining the potential issues with the use of hand-held XRF to test for LPCL compliance in WEEE due to the more frequent presence of TBBP-A and other as yet unidentified compounds in such items.

4.2 Accuracy and Precision of XRF-Determined Bromine as a Surrogate for POP-BFRs

Upon comparing the results of total Br from portable XRF analysis with compound-specific mass spectrometry, the overall *accuracy* of XRF strongly depends on the type of polymer under investigation. Though the regression of all sample-groups appears to follow a generally linear correlation between XRF and MS results, the deviation of the slopes from unity in most

of the plastic types indicates that matrix effects occur prominently in low-density materials. Br concentrations obtained from XRF measurements were adjusted based on subsequent mass spectrometric analyses of the same samples thus allowing for a correction factor to be inferred (*Section 3.2*). However, for use of this instrument as a standalone analyser for accurately quantifying total bromine concentrations in the range of materials studied here, suitable calibration standards unique to each type of polymer (ABS, HIPS, PUF, etc.) would initially be required to ensure reliable compensation for matrix effects. Application of correction factors to XRF measurements discerned following MS analysis was successful in correcting the overall accuracy of the instrument for all measured concentrations, with little effect on the deviations for individual measurements.

These corrections had little effect on the deviations for individual measurements however; therefore, the estimated *precision* of the instrument still requires further refinement. In all but one of the sample groups studied, the deviation of XRF analysis from the MS-determined bromine content of the samples significantly exceeded a 95 % confidence interval. These variations may be due to the elemental and chemical composition of individual samples interfering with XRF analyses in ways unique to each sample. Additionally, as shown by the occurrence of background interference in WEEE samples (*S4*), the penetration-depth of x-rays is not finite as they permeate through thin plastic items to the substrate material thereby skewing estimations of the sample's density by the instrument (*Section 3.2.1*).

As shown earlier, further uncertainties may be attributable in some cases to the presence in samples of BFRs not targeted herein. The presence of these other BFRs (or other bromine-based compounds) also acts as an obstacle to the more effective use of XRF an accurate metric of POP-BFR concentrations (*Figure 1*). This is mainly due to the inherent lack of selectivity of XRF, which renders it incapable of distinguishing between POP-BFRs and other bromine-containing compounds contributing to the total Br concentration. The precise

detection of POP-BFRs by XRF will be exacerbated further by the presence of multiple BFRs within the same sample-groups by the further-use of nBFRs.

Based on the present study, EPS and XPS constitute the groups which could most reliably utilise XRF-quantified bromine as a surrogate for POP-BFRs *in situ* at recycling sites, showing the highest number of samples with the lowest deviations from true bromine content. Both groups would require specific calibration to compensate for matrix effects and improve the overall accuracy of analyses. In its current state, XRF-determined bromine measurements are unsuitable as a surrogate for POP-BFR determination in the remaining sample groups investigated herein. Refinements to measurement protocols (*e.g.* material separation to avoid background interference in WEEE) and the inclusion of reference standards specific to each type of plastic could improve the accuracy of the XRF instrument. However, specific matrix effects inherent in low density materials, varying chemical composition of the analyte materials, and the presence of non-POP-BFRs, and the lack of specificity of XRF in determining bromine species constitute substantial obstacles to the standalone use of XRF for the accurate quantification of POP-BFRs in plastic media.

5. Conclusions

Our study clearly shows that portable XRF cannot be used to accurately determine absolute concentrations of POP-BFRs. However, its use as a screening tool for LPCL compliance appears to be viable, provided sufficient prior knowledge of typical BFR-treatment in different plastics is available and the number of samples misclassified as exceeding LPCLs is deemed acceptable or can be reduced. Of particular note is the applicability of XRF for screening EPS and XPS materials above the proposed LPCL threshold (710 mg kg⁻¹) due to the observed high precision shown for quantifying POP-BFRs in these materials. However,

the results obtained from the standalone use of XRF measurements as a surrogate for POP-BFR determination in the other plastic types investigated agree with conclusions previously reached by Gallen et al. (2014) and Petreas et al. (2016), namely that significant inconsistencies between measurement techniques result in XRF alone being insufficient to precisely determine BFRs, furthermore requiring MS to identify concentrations of specific BFRs. Application of reference standards such as those utilized by Guzzonato et al. (2016) can further enhance the accuracy of XRF as a surrogate measure of BFR concentrations. Restricting screening solely to non-WEEE items further reduces the frequency of false positives to 2.5 %. To ensure that waste plastics are being recycled effectively and safely, the validity of XRF screening for compliance with LPCLs for POP-BFRs should remain an ongoing field of investigation, in particular with respect to matrix effects and the need for calibration standards, and the expected further use of NBFRs in recyclable plastics.

In summary, our study shows that while portable XRF may be used as a reliable (though not infallible) “pass-fail” indicator of compliance with LPCLs for POP-BFRs. We also show that refinements to measurement protocols (*e.g.* material separation to avoid background interference in WEEE) and the inclusion of reference standards specific to each type of plastic could potentially reduce the incidence of “false positives” resulting from use of portable XRF, thereby diminishing the number of waste items incorrectly identified as requiring special treatment.

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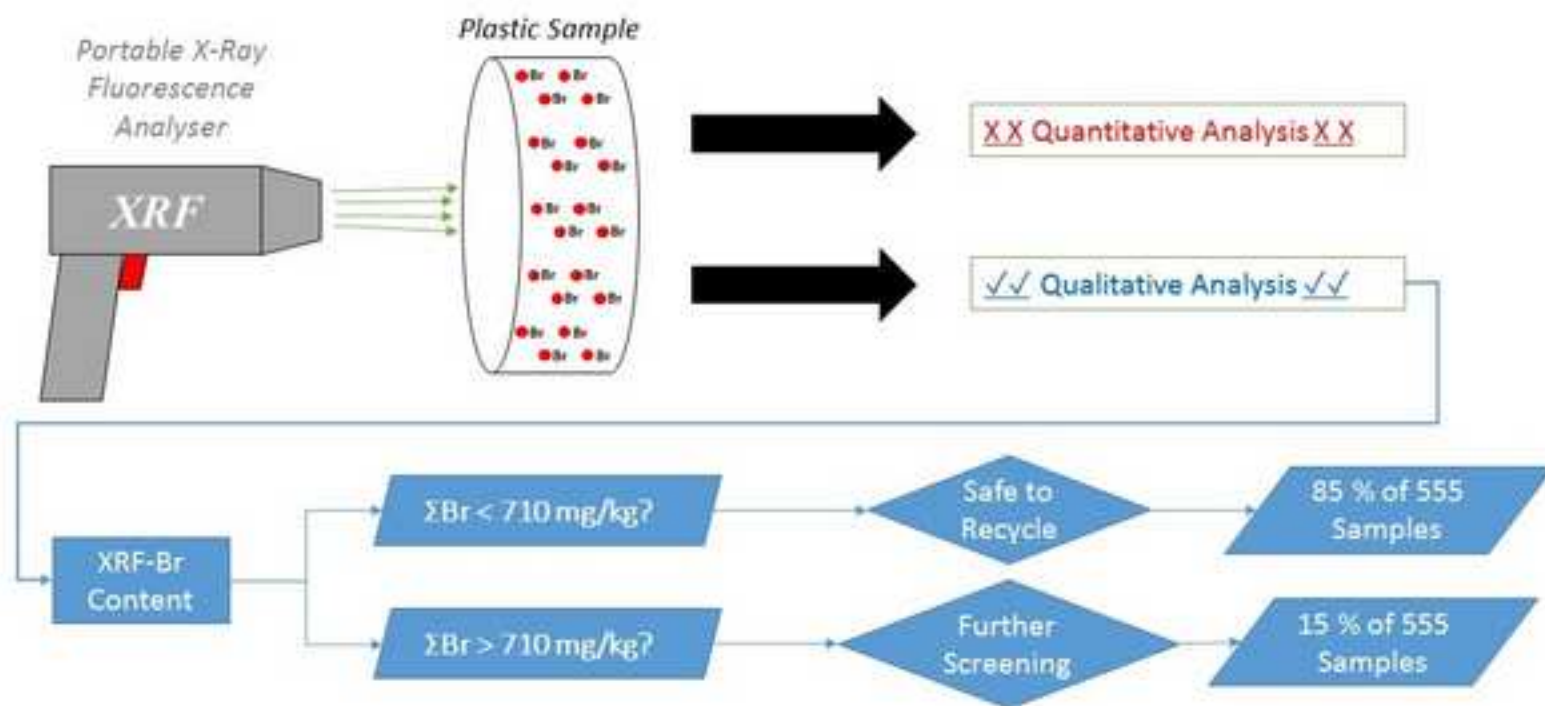
549 **References**

- 550 ABDALLAH, M. A.-E., DRAGE, D. S., SHARKEY, M., BERRESHEIM, H. & HARRAD, S. 2017. A rapid
 551 method for the determination of brominated flame retardant concentrations in plastics and
 552 textiles entering the waste stream. *Journal of Separation Science*, 40, 3873-3881.
- 553 ABDALLAH, M. A.-E., IBARRA, C., NEELS, H., HARRAD, S. & COVACI, A. 2008. Comparative evaluation
 554 of liquid chromatography–mass spectrometry versus gas chromatography–mass
 555 spectrometry for the determination of hexabromocyclododecanes and their degradation
 556 products in indoor dust. *Journal of Chromatography A*, 1190, 333-341.
- 557 AL-OMRAN, L. & HARRAD, S. Distribution patterns of legacy and "novel" brominated flame
 558 retardants in different particle size fractions of indoor dust in Birmingham, UK. 10th
 559 Network Conference on Persistent Organic Pollutants (POPs): Environmental Organic
 560 Pollutants, Metabolites and Transformation Products, 13th April 2016 2016 Winterbourne
 561 House and Garden, University of Birmingham. 10th Network Conference on POPs.
- 562 ALDRIAN, A., LEDERSTEGER, A. & POMBERGER, R. 2015. Monitoring of WEEE plastics in regards to
 563 brominated flame retardants using handheld XRF. *Waste Manag*, 36, 297-304.
- 564 DRAGE, D., SHARKEY, M., ABDALLAH, M. A., BERRESHEIM, H. & HARRAD, S. 2018. Brominated flame
 565 retardants in Irish waste polymers: Concentrations, legislative compliance, and treatment
 566 options. *Science of The Total Environment*, 625, 1535-1543.
- 567 EC 2004. EC regulation no. 850/2004 of the European Parliament and of the Council of 29 April 2004
 568 on persistent organic pollutants and amending Directive 79/117/EEC. *OJL*, 158, 7.
- 569 EC 2010. Commission regulation no 756/2010 of 24 August 2010 amending regulation (EC) No
 570 850/2004 of the European Parliament and of the Council on persistent organic pollutants as
 571 regards Annexes IV and V. 223, 20.
- 572 EC 2011. Final Report: Study on waste related issues of newly listed POPs and candidate POPs. *In*:
 573 (ESWI), E. T. T. S. W. I. (ed.). Munich: European Commission.
- 574 EC 2016. Commission regulation (EU) 2016/460 of 30 March 2016 amending Annexes IV and V to
 575 regulation No 850/2004 of the European Parliament and of the Council on persistent organic
 576 pollutants. *Off. J. Eur. Commun*.
- 577 EPA. 2016. *WEEE Statistics for Ireland* [Online]. Environmental Protection Agency of Ireland.
 578 Available:
 579 [http://www.epa.ie/pubs/reports/waste/stats/weeedata2013/EPA_WEEE_2013_data_releas](http://www.epa.ie/pubs/reports/waste/stats/weeedata2013/EPA_WEEE_2013_data_release_web.pdf)
 580 [e web.pdf](http://www.epa.ie/pubs/reports/waste/stats/weeedata2013/EPA_WEEE_2013_data_release_web.pdf) [Accessed 07-03-18 2018].
- 581 EU 2017a. COMMISSION REGULATION (EU) 2017/227 of 9 February 2017 amending Annex XVII to
 582 Regulation (EC) No 1907/2006 of the European Parliament and of the Council concerning the
 583 Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH) as regards
 584 bis(pentabromophenyl)ether *Official J Eur Union*, 35, 6-9.
- 585 EU 2017b. COUNCIL REGULATION (EU) 2017/997 of 8 June 2017 amending Annex III to Directive
 586 2008/98/EC of the European Parliament and of the Council as regards the hazardous
 587 property HP 14 'Ecotoxic'. *Official Journal of the European Union*, 150, 1-4.
- 588 GALLEN, C., BANKS, A., BRANDSMA, S., BADUEL, C., THAI, P., EAGLESHAM, G., HEFFERNAN, A.,
 589 LEONARDS, P., BAINTON, P. & MUELLER, J. F. 2014. Towards development of a rapid and
 590 effective non-destructive testing strategy to identify brominated flame retardants in the
 591 plastics of consumer products. *Sci Total Environ*, 491-492, 255-65.
- 592 GROSSE, Y., LOOMIS, D., GUYTON, K. Z., EL GHISSASSI, F., BOUVARD, V., BENBRAHIM-TALLAA, L.,
 593 MATTOCK, H. & STRAIF, K. 2016. Carcinogenicity of some industrial chemicals. *The Lancet*
 594 *Oncology*, 17, 419-420.

- GUZZONATO, A., PUYPE, F. & HARRAD, S. J. 2016. Improving the accuracy of hand-held X-ray fluorescence spectrometers as a tool for monitoring brominated flame retardants in waste polymers. *Chemosphere*, 159, 89-95.
- IPCS. 1997. *Flame retardants (EHC 192, 1997)* [Online]. World Health Organisation. Available: <http://www.inchem.org/documents/ehc/ehc/ehc192.htm> [Accessed March 14 2016].
- MALKOSKE, T., TANG, Y., XU, W., YU, S. & WANG, H. 2016. A review of the environmental distribution, fate, and control of tetrabromobisphenol A released from sources. *Science of The Total Environment*, 569-570, 1608-1617.
- MARVIN, C. H., TOMY, G. T., ARMITAGE, J. M., ARNOT, J. A., MCCARTY, L., COVACI, A. & PALACE, V. 2011. Hexabromocyclododecane: Current Understanding of Chemistry, Environmental Fate and Toxicology and Implications for Global Management. *Environmental Science & Technology*, 45, 8613-8623.
- MORF, L., TAVERNA, R., DAXBECK, Z. H. & SMUTNY, R. 2003. Selected polybrominated flame retardants PBDEs and TBBPA: Substance flow analysis. *Environmental Series No 338: Environmentally Hazardous Substances*.
- PETREAS, M., GILL, R., TAKAKU-PUGH, S., LYTLE, E., PARRY, E., WANG, M., QUINN, J. & PARK, J.-S. 2016. Rapid methodology to screen flame retardants in upholstered furniture for compliance with new California labeling law (SB 1019). *Chemosphere*, 152, 353-359.
- PETTY, S., LINDEMAN, A. E., BLUM, A., BELLUR, S., DIAMOND, M. L., LUCAS, D., KOSHLAND, C. P. & WEBER, R. MANAGEMENT OF HALOGENATED FLAME RETARDED WASTES IN THE UNITED STATES –THE NEED FOR A CIRCULAR ECONOMY APPROACH. 36th International Symposium on Halogenated Organic Pollutants, 28th August 2016 2016 Palazzo Dei Congressi, Firenze. 36th International Symposium on Halogenated Organic Pollutants.
- RAUERT, C., HARRAD, S., SUZUKI, G., TAKIGAMI, H., UCHIDA, N. & TAKATA, K. 2014. Test chamber and forensic microscopy investigation of the transfer of brominated flame retardants into indoor dust via abrasion of source materials. *Sci Total Environ*, 493, 639-48.
- RAUERT, C., KURIBARA, I., KATAOKA, T., WADA, T., KAJIWARA, N., SUZUKI, G., TAKIGAMI, H. & HARRAD, S. 2016. Direct contact between dust and HBCD-treated fabrics is an important pathway of source-to-dust transfer. *Science of The Total Environment*, 545-546, 77-83.
- SCHLUMMER, M., VOGELSANG, J., FIEDLER, D., GRUBER, L. & WOLZ, G. 2015. Rapid identification of polystyrene foam wastes containing hexabromocyclododecane or its alternative polymeric brominated flame retardant by X-ray fluorescence spectroscopy. *Waste Manag Res*, 33, 662-70.
- SINDIKU, O., BABAYEMI, J., OSIBANJO, O., SCHLUMMER, M., SCHLUEP, M., WATSON, A. & WEBER, R. 2015. Polybrominated diphenyl ethers listed as Stockholm Convention POPs, other brominated flame retardants and heavy metals in e-waste polymers in Nigeria. *Environmental Science and Pollution Research*, 22, 14489-14501.
- UNEP 2009. Stockholm Convention on Persistent Organic Pollutants (as amended 2009). In: UNEP (ed.). Stockholm, Sweden: United Nations Environment Programme.
- UNEP 2010. Technical review of the implications of recycling commercial pentabromodiphenyl ether and commercial octabromodiphenyl ether. In: COMMITTEE, P. O. P. R. (ed.). Geneva: United Nations Environmental Programme.
- UNEP 2013. An amendment to Annex A adopted by the Conference of the Parties to the Stockholm Convention on Persistent Organic Pollutants at its sixth meeting (Decision SC-6/13). In: UNEP (ed.). Stockholm, Sweden: United Nations Environment Programme.
- UNEP 2017a. COP-8/32: Report on the Conference of Parties to the Stockholm Convention on persistent Organic Pollutants on the works of its eighth meeting. In: UNEP (ed.). Geneva, Switzerland: United Nations Environment Programme.
- UNEP 2017b. Guidance for the inventory of Hexabromocyclododecane (HBCD). In: PROGRAMME, U. N. E. (ed.) SC-7/10. Switzerland: Secretariat of the Stockholm Convention.

- 645 WEIL, E. D. & LEVCHIK, S. V. 2009. Flame Retardants in Commercial Use of Development for Textiles.
646 *Journal of Fire Sciences*, 26, 243-281.
647 ZAWISZA, R. S. B. 2012. Quantification in X-Ray Fluorescence Spectrometry. *In*: SHARMA, S. K. (ed.)
648 *X-Ray Spectroscopy*. InTech.

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Highlights

- XRF viable check of compliance of some waste categories within legislative limits
- XRF incorrectly reports legislative limits exceeded in only 6 % of samples
- Restricted to non-WEEE items, XRF incorrectly reports only 2.5 % of samples
- Accurate quantification of POP-BFRs via XRF not feasible for most waste types
- XRF quantification of POP-BFRs unreliable due to TBBP-A, NBFRs and matrix effects

1 Portable X-Ray Fluorescence for the Detection of POP-BFRs
2 in Waste Plastics

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Abstract

The purpose of this study was to establish the efficacy of portable x-ray fluorescence (XRF) instrumentation as a screening tool for a variety of end of life plastics which may contain excess amounts of brominated flame retardants (BFRs), in compliance with European Union (EU) and United Nations Environment Programme (UNEP) legislative limits (low POP concentration limits – LPCLs). 555 samples of waste plastics were collected from eight waste and recycling sites in Ireland, including waste electrical and electronic equipment (WEEE), textiles, polyurethane foams (PUFs), and expanded polystyrene foams. Samples were screened for bromine content, *in situ* using a Niton™ XL3T GOLDD XRF analyser, the results of which were statistically compared to mass spectrometry (MS)-based measurements of polybrominated diphenyl ethers (PBDEs), hexabromocyclododecane (HBCDD) and tetrabromobisphenol-A (TBBP-A) concentrations in the same samples.

Regression between XRF and MS for WEEE samples show that, despite an overall favourable trend, large deviations occur for a cluster of samples indicative of other bromine-based compounds in some samples; even compensating for false-positives due to background interference from electronic components, XRF tends to over-estimate MS-determined BFR concentrations in the 100 to 10,000 mg kg⁻¹ range. Substantial deviations were additionally found between results for PUFs, textiles and polystyrene samples, with the XRF over-estimating BFR concentrations by a factor of up to 1.9; this is likely due to matrix effects influencing XRF measurements. However, expanded (EPS) and extruded polystyrene (XPS) yielded much more reliable estimations of BFR-content due to a dominance of HBCDD in these materials.

XRF proved much more reliable as a “pass/fail” screening tool for LPCL compliance (including a prospective LPCL on Deca-BDE based on REACH). Using a conservative threshold of BFR content exceeding legislative limits (710 mg kg⁻¹ bromine attributed to

38 penta-BDE), XRF mistakenly identifies only 6 % of samples (34/555) as exceeding
39 legislative limits.

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41 **Keywords**

42 Waste Plastics; LPCL Screening; Quantification; PBDEs; HBCDD.

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1. Introduction

Polybrominated diphenyl ethers (PBDEs) and hexabromocyclododecane (HBCDD) are two groups of brominated flame retardants (BFRs) which have been extensively applied to various commercial and consumer products to meet flammability standards. HBCDD has been used as a flame retardant additive in expanded (EPS) and extruded (XPS) polystyrene insulation foams as well as in high impact polystyrene (HIPS) for electrical housing and junction boxes, as well as a textile coating agent for furniture and furnishings (Marvin et al., 2011, UNEP, 2017b). Of the three commercial PBDE formulations, Penta-BDE is reportedly almost exclusively used in polyurethane foams (PUFs) for domestic, office and automotive applications, along with minor applications in printed circuit boards and microprocessors in electrical and electronic equipment (EEE) (UNEP, 2010). Octa-BDE has been applied to acrylonitrile butadiene styrene (ABS) and HIPS, largely used as casings for EEE (EC, 2011). Deca-BDE was commonly used in coating agents applied to the surfaces of textiles and upholstery as well as applied to HIPS for EEE as an additive compound (Weil and Levchik, 2009, IPCS, 1997). Over the last two decades however, concerns about their toxicity, persistence and ability to bioaccumulate has led to their listing as persistent organic Pollutants (POPs) under the Stockholm Convention. The commercial mixtures of Penta- and Octa-BDE were listed in 2009 (UNEP, 2009), whilst HBCDD was listed in 2013 (UNEP, 2013), and the Deca-BDE commercial mixture listed in 2017 (UNEP, 2017a). Another common legacy BFR, tetrabromobisphenol-A (TBBP-A), is also extensively used in as an additive in HIPS and ABS and also reactively added to printed circuit boards for EEE (Morf et al., 2003, IPCS, 1997). Though not currently under consideration for listing as a POP, TBBP-A has been recently classified as H410 (very toxic to aquatic species), and listed as a Class 2A carcinogen (Grosse et al., 2016, Malkoske et al., 2016). Additionally, waste articles

containing TBBP-A at concentrations in excess of 0.1 % is to be classified as “hazardous waste” (EU, 2017b).

In the light of growing environmental concern, measures are being adopted in order to prevent further environmental contamination from goods which were treated with POP-BFRs (UNEP, 2009, EC, 2004). One such measure is the modification of recycling systems to include screening procedures for goods suspected to contain high concentrations of POPs, including POP-BFRs. Low POP concentration limits (LPCLs) of 1000 mg kg⁻¹ have been established for each of the HBCDD, Penta-BDE and Octa-BDE commercial mixtures (EC, 2010, EC, 2016, EU, 2017a), in addition to a limit on Deca-BDE to come into force in 2019 (EU, 2017). However, a fast and cost-effective method of identifying products exceeding these limits has not yet been identified, with industry standards (such as conventional chromatographic-mass spectrometric techniques) being impractical for this purpose due to their high running costs and low throughput.

Recently the use of portable x-ray fluorescence (XRF) measurements of elemental Br has been suggested as a surrogate measure of POP-BFR concentrations. Several studies have been performed to investigate the efficacy of portable XRF for the measurements of BFRs in various plastic products, including EEE (Gallen et al., 2014, Aldrian et al., 2015, Guzzonato et al., 2016) and furniture fabrics, foams and textiles (Petreas et al., 2016). Whilst these studies have had varying degrees of success, they have all concluded that XRF-based measurements are not capable of accurately quantifying concentrations of specific BFRs as XRF measures elemental bromine only. However, Aldrian et al. (2015) and Petreas et al. (2016) suggested that the use of XRF may be an effective screening tool for bromine content in WEEE and furniture, as well as Schlummer et al. (2015) concluding effective screening potential of HBCDD with the inclusion of an extraction process to distinguish the Br species. Furthermore, Guzzonato et al. (2016) demonstrated that the accuracy of XRF measurements

of Br in ABS and HIPS may be improved by use of custom-made solid reference standards containing Deca-BDE, and concluded that use of XRF to screen waste electrical and electronic equipment (WEEE) for compliance with LPCLs was feasible. The largest recent study (Sindikú et al., 2015) includes XRF screening in their methodology using varying ranges of Br content, proving relatively successful in screening for BFR-content (with an instrumental precision of $\pm 20\%$) but does highlight limitations in discerning the species of bromine.

While the suitability of the XRF as a tool for predicting BFR concentrations has been evaluated previously, many of the studies hitherto have been on a relatively small scale (<50 samples). Moreover, the range of plastics previously studied is limited to a few types and applications or do not show in-depth comparisons of the accuracy and precision of XRF with respect to MS analysis. In light of the introduction of LPCLs and the substantial mass of waste polymers that will require screening for compliance with LPCLs (*e.g.* 42,628 tonnes of WEEE collected in Ireland in 2013 (EPA, 2016)), it is vital that a rapid screening method is developed to enable fast and reliable identification of waste items exceeding LPCLs. Therefore the aims of this study are to (i) examine the efficacy of portable XRF measurements as a predictor of BFR concentrations in a wide range of plastics in the waste stream; and (ii) to determine whether portable XRF can be used as a “pass/fail” screening tool for the interception of waste products exceeding LPCLs. These aims were achieved by a large scale sampling campaign of recyclable plastics at waste and recycling sites in Ireland. XRF measurements of bromine in a variety of waste articles (including WEEE plastics, domestic and end of life vehicle (ELV) soft furnishings (PUF and upholstery fabrics) and EPS/XPS insulation) were taken prior to quantitative analysis of selected BFRs via either GC/MS or LC-MS/MS. To our knowledge, this is the first assessment of XRF as a tool for monitoring compliance with LPCL legislation. Moreover, it represents the most

comprehensive assessment to date of the accuracy and suitability of hand-held XRF analysis for quantification of BFR levels in waste articles.

2. Materials and Methods

2.1 Materials

Chemical standards for native BDEs -28, -47, -77, -99, -100, -128, -153, -154, -183, -196, -197, -203, -209, native α -HBCDD, β -HBCDD, γ -HBCDD, $^{13}\text{C}_{12}$ -BDE-209, $^{13}\text{C}_{12}$ - α -HBCDD, $^{13}\text{C}_{12}$ - β -HBCDD, $^{13}\text{C}_{12}$ - γ -HBCDD, d_{18} - γ -HBCDD and $^{13}\text{C}_{12}$ -TBBP-A were purchased from Wellington Laboratories (Guelph, ON, Canada). PCB-129 was purchased from Accustandard (New Haven, CT, USA). All solvents (HPLC grade hexane, dichloromethane (DCM), iso-octane and methanol) and sulfuric acid (>95 %) were purchased from Fisher Scientific (Loughborough, UK).

2.2 Sample Collection and Field Measurement

Samples were obtained from eight waste and recycling sites in Ireland and their bromine concentrations measured *in situ* using a hand-held XRF device. Samples from a range of different waste categories were collected: HIPS and ABS hard plastic casings from WEEE; soft furnishings and textiles typical in both domestic and vehicular environments; and polystyrene foams from building insulation and packaging materials. Following collection and XRF analysis, destructive chemical analysis via GC-MS and LC-MS/MS was carried-out on small sub-samples taken from the same parent product, within the immediate vicinity of the area subjected to XRF analysis. This was performed to evaluate the accuracy with which

the XRF-determined bromine concentrations correlated with those of GC/MS or LC-MS/MS measurements of selected BFRs.

In total, matched Br and BFR measurements were obtained for 555 samples; *Table 1* provides an overview of the number of samples collected from each “waste type”. Following on-site use of the XRF instrument, small sections of the scanned areas ($\sim 1\text{-}2\text{ cm}^2$ for HIPS/ABS, upholstery and textiles, or $\sim 1\text{-}2\text{ cm}^3$ for polystyrene and PUF) were subsequently removed and individually stored in labelled polyethylene bags. These collected samples were then shipped to the University of Birmingham where concentrations of POP-BFRs and TBBP-A were determined.

2.3 XRF Analysis

Each measurement involved placing the XRF instrument directly on to the measurement surface, with the operator standing directly behind the instrument for the duration of the measurement. As per Niton UK guidelines on the use of the device, secondary x-rays projected from the specimen deviate at angles around the device (mostly laterally) as well as at much lower intensities than primary x-rays, thus attenuating rapidly. Using the secondary dose rates produced during plastics mode of operation, on plastic materials, and with varying substrates (air, concrete, wood, etc.), the maximum dose for the user (at the device’s trigger) was calculated for the sum of all measurements carried out and found to be well-below the annual dose for a category B radiation worker (*i.e.* $<20\text{ mSv in any single year}$).

Determination of total bromine content in the samples was carried out *in situ* using a Niton *XLt3-900 GOLDD X-Ray Fluorescence Analyser*. Calibration was performed by Niton UK using proprietary standards containing varying concentrations of relevant inorganic compounds in a polymer matrix. Quantification and qualification of bromine for the Niton

XL3t model are achieved using the K α_1 line (11.9242 eV) and K α_2 line (11.8776 eV) respectively. The instrument was operated in the “plastics” mode of operation, which optimises the instrument’s settings for interaction of x-rays with low density polymer materials and quantification of specific elements in their matrices. Standard analyses using the XRF instrument in this mode gives a 95 % confidence interval ($CI = \pm 2\sigma$) with each measurement taken. The duration of analysis ranged from 30 to 105 seconds with longer iterations required to improve instrumental uncertainty in samples with high bromine content and for samples comprising of low density materials (Zawisza, 2012).

For HIPS, ABS and insulation foam samples, the surface of the material was wiped with a clean non-fibrillating tissue prior to analysis, in order to remove sediment and dust which could interfere with the instrument’s primary x-rays or may contain traces of bromine. A thickness correction of 2 mm was additionally applied to the HIPS and ABS samples to help account for the finite thickness of the samples (per manufacturer guidelines); this reduces the risk of interference from substrate materials as the instrument internally estimates the density of an analyte based on Compton scattering of primary x-rays. The instrument window was then placed flat against the sample surface and a measurement of bromine content carried out (with a minimum thickness of 10 cm for insulation samples and as presented at approximately 2 mm for HIPS and ABS samples). Upholstery and other soft furnishings were manually folded, compressed to a thickness of approximately 3 cm (to achieve the thickness required for said materials for full attenuation of primary x-rays, per instrument manufacturer guidelines) and held in place by placing the instrument over the sample, in order to increase the density of the active analysis zone. Three repeat measurements were carried out on each sample, several centimetres apart from each scanning point and at varying orientations. These repeat measurements were required to be carried out on the same plastic panel/area and under

the same experimental conditions in order to detect instances of heterogeneous distribution of BFRs within the body of sample.

Additional XRF measurements of bromine concentrations on available sub-samples of WEEE HIPS and ABS samples (i.e. those aliquots removed for BFR determination) were carried out in a controlled laboratory setting. These measurements were made in order to determine the instances where bromine detected during field measurements were due to background interference, being attributed to the presence of bromine in underlying electronic components rather than from the polymeric casing itself.

2.4 Extraction and Clean-Up

For quantitative analysis of BFRs, samples were extracted and cleaned according to methods previously described (Abdallah et al., 2017). Briefly, aliquots of samples (20-100 mg) were cut with a retractable blade and weighed directly into a 15 mL glass centrifuge tube and spiked with 20 ng of BDEs -77 and -128, $^{13}\text{C}_{12}$ - α -, $-\beta$ -, and γ -HBCDD, $^{13}\text{C}_{12}$ -TBBP-A, and 40 ng $^{13}\text{C}_{12}$ -BDE-209 as internal standards. Approximately 3 mL of dichloromethane (DCM) was added to the aliquot and vortexed for 2 minutes, followed by 30 minutes sonication. The extraction process was repeated three times with the combined extracts collected in a separate glass centrifuge tube. Crude extracts were concentrated under a gentle stream of N_2 to near-dryness and reconstituted in 2 mL hexane. Extracts were washed with >95 % sulfuric acid and supernatant organic layer was collected and concentrated to near-dryness under a gentle N_2 stream. Samples were reconstituted in 200 μL of iso-octane containing 0.2 ng μL^{-1} PCB-129 as a recovery standard. After determination of PBDEs via GC-MS, extracts were reconstituted in methanol containing 0.2 ng μL^{-1} d_{18} - γ -HBCDD for determination of HBCDDs and TBBP-A via LC-MS/MS analysis.

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213 **2.5 Mass Spectrometric Analysis**

214 Quantitative analysis of PBDEs was performed in a single injection on a ThermoFisher Trace
215 1310 gas chromatograph coupled to a ThermoFisher ISQ mass spectrometer (MS). The MS
216 was operated in electron ionisation mode using selective ion monitoring (SIM). One μL of
217 the purified extract was injected for analysis using a programmable temperature vapouriser
218 (PTV) onto a Restek Rxi-5Sil MS column (15m x 0.25 mm x 0.25 μm film thickness).
219 Helium was used as the carrier gas at a flow rate of 1.5 mL min^{-1} . Full GC/MS parameters
220 have been reported previously (Abdallah et al., 2017).

221 HBCDDs were measured using a Shimadzu LC-20AB Prominence binary pump liquid
222 chromatograph equipped with a Sil-20A auto sampler and a DGU-20A3 vacuum degasser
223 coupled to an AB Sciex API 2000 triple quadrupole MS. Chromatographic separation was
224 achieved using Agilent Pursuit XRS3 C18 column (150 mm x 2 mm, I.D., 3 μm particle size)
225 and a mobile phase of (a) 1:1 methanol/water and (b) methanol at a flow rate of $180 \mu\text{L min}^{-1}$.
226 Molecular ionisation was achieved using an electrospray ionisation (ESI) source operated in
227 negative ion mode. The MS/MS was operated in the multiple reaction monitoring (MRM)
228 mode. The MRMs transitions monitored were on m/z $640.6 \rightarrow 79$, m/z $652.4 \rightarrow 79$ and m/z
229 $657.7 \rightarrow 79$ for the native and the $^{13}\text{C}_{12}$ -labelled HBCDD diastereomers respectively and
230 $540.8 \rightarrow 79$, m/z $552.8 \rightarrow 79$ were used to monitor native and $^{13}\text{C}_{12}$ -labelled TBBP-A. Full
231 LC-MS/MS parameters have been reported previously (Abdallah et al., 2008).

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233 **2.6 Quality Assurance/Quality Control**

234 For BFR analysis, a reagent blank consisting of 100 mg of anhydrous sodium sulfate was
235 analysed with every batch of 11 samples. "Control" samples were created using plastics and

textiles that contain no BFRs and were also analysed throughout the study; three Controls were assessed for each matrix. None of the target compounds were found above the limits of detection in the blanks. Therefore results were not corrected for blank residues and method limits of detection (LOD) and quantification (LOQ) were estimated based on a signal to noise ratio (S/N) of 3:1 and 10:1 respectively.

Method accuracy and precision was assessed via repeated analysis of certified reference materials (CRMs) ERM-EC591 (polypropylene), ERM-EC590 (polyethylene) in addition to textiles (polyester fabrics), extruded polystyrene and expanded polystyrene that have been previously measured by this laboratory and another. All values were found to be close to certified or indicative levels, with a relative standard deviation of <15 % (Abdallah et al., 2017).

2.7 Exclusion Criteria for Regression Analysis

The regression analysis comprised a comparison between XRF-determined bromine, and the equivalent bromine concentrations attributed to quantified BFRs (see supporting information, S2). However, the accuracy of the XRF instrument must be taken into consideration for the regression between its results of bromine concentrations and those from the mass spectrometric analyses. The XRF instrument displays as a 95 % confidence interval or ± 2 standard deviations ($\pm 2\sigma$) for each analysis carried out; although this value can be altered, it provides a sufficiently concise confidence interval to establish the stability of analyses.

During the analysis of EPS and XPS foam samples using the XRF device, a $\pm 2\sigma$ interval as high as 16 mg kg⁻¹ bromine occurred with a “null” reading (i.e. the value determined by the XRF instrument was 0 ± 16 mg kg⁻¹), thus a conservative 20 mg kg⁻¹ value was chosen as the XRF analyser’s limit of detection (LOD_X). For the remaining polymeric materials – PUF,

HIPS, ABS, upholstery, textiles – a LOD_X of 10 mg kg^{-1} was chosen using the same criteria as established for XPS and EPS samples (with a $\max \pm 2\sigma$ interval of 8 mg kg^{-1} for these sample groups). Therefore, in instances where each of the triplicate XRF measurements conducted on each sample fell below the LOD_X , that sample was not considered for the regression analysis. If, however, one of the triplicate measurements was above the LOD_X (and even if the average was below), the sample was included, in consideration of possible non-uniform BFR distribution throughout the body of the sample.

3. Results

3.1 Total Bromine Concentrations Determined by XRF Analyses

Table 1 shows a summary of the bromine concentrations quantified using the XRF during *in situ* analyses. Highest bromine concentrations were detected in the WEEE waste category at $110,000 \text{ mg kg}^{-1}$ and $150,000 \text{ mg kg}^{-1}$ in IT & Telecoms and Display samples respectively. Very high concentrations (exceeding $10,000 \text{ mg kg}^{-1}$) were also detected in the Furniture Upholstery, ELV Upholstery, and ELV (other) sample groups. The Fridge/Freezer, Curtain, C&D XPS, Mattress Foam and Mattress Upholstery sample groups showed very low maximum Br concentrations ($< 1,000 \text{ mg kg}^{-1}$) along with low median and mean values. This indicates that these sample groups underwent low levels of treatment with bromine-containing compounds, and/or experienced transfer of bromine-containing compounds while in use or during storage for recycling/transfer (Rauert et al., 2014). The remaining sample groups showed maximum bromine content between $1,000$ and $10,000 \text{ mg kg}^{-1}$ which, along with the aforementioned groups with concentrations in samples reaching roughly $150,000 \text{ mg kg}^{-1}$ Br, demonstrates potential from some articles in these groups to exceed LPCLs. However, as is evidenced by the low median concentrations for the sample groups relative to

the maximum values, samples with excessively high concentrations of bromine make up a minority of each remaining sample group. This indicates a relatively low proportion of waste articles potentially treated with POP-BFRs in these sample groups (with the possible exception of Display, Furniture Foam, Furniture Upholstery, and Vehicle Foam samples groups).

We have additionally observed so-called “false-positives” in different waste categories. A “false positive” corresponds to a situation where the XRF measurement of Br indicates the LPCL for a POP-BFR to be exceeded, but the POP-BFR concentration is below the LPCL. By comparison, a “false negative” would occur where the POP-BFR concentration is above the LPCL, but this is not indicated by the XRF measurement of Br. These occurrences will be reported by waste category in the following sections.

3.2 XRF – MS Total Bromine Measurement Comparison

Concentrations of BFRs in the samples included in this study have been previously reported by Drage et al. (2018). For comparison with XRF measurements they have been briefly outlined in *Table 1*. Additionally, following MS-analysis of the collected samples, some sample groups including the Mattress, Curtain, Carpet, ELV (other), Fridge/Freezer, and ELV (other) sample groups showed either no excessive concentrations of BFRs or very few samples with excess concentrations. These groups were therefore considered unsuitable to act as comparative metrics for regressions between MS and XRF analyses.

3.2.1 – WEEE Hard Plastics

In addition to the 65 WEEE samples excluded based on $Br < LOD_x$ (*Section 2.7*), a further 15 samples were omitted from the regression analysis due to laboratory confirmation of a background interference during *in situ* measurements of the samples (*Section 2.3*). *Table 2*

shows the results obtained for these 15 samples, comparing the average of the on-site triplicate XRF measurements to lab-based duplicate XRF measurements, the latter more accurately equating to the actual concentrations of bromine in the samples.

Application of this additional exclusion criterion yielded a final data set of 70 ABS/HIPS samples remaining for regression analysis, the result of which is shown in *Figure 1*. The linear regression coefficient (slope, m) is 0.98 and the coefficient of determination (R^2) is 0.614. However, a notable cluster of samples ($n = 10$) show much higher concentrations of bromine as determined by XRF analysis compared to the concentrations determined by GC/MS / LC-MS/MS analysis (defined here as “true” Br content). *Figure 2 (a)* is a Bland-Altman plot showing the variation in the Br content determined via XRF analysis as a percentage of true Br content $[(XRF-MS)/MS] \times 100$, where it can be seen that these outliers show at least a 4.9-fold overestimation of “true” Br content (z-test, $p < 0.001$) compared to a maximum of 2.4-fold overestimation in the remainder. It is likely therefore that these samples contained bromine in BFR-type chemicals other than those analysed for by the MS methods used herein, such as BTBPE, tetrabromophthalic acid, and DPDPE (Al-Omran and Harrad, 2016, Petty et al., 2016, IPCS, 1997).

Figure 2 (b) highlights large variations still exist between Br concentrations obtained for the same samples via the two measurement techniques. Samples with similar concentrations of BFRs show varying deviations between the techniques such that even employment of a correction factor would have limited success in improving the regression, across all concentrations shown herein. For example, samples with total Br concentrations ranging between 100 and 1,000 mg kg^{-1} show deviations from -3 % to +250 % between the analysis techniques for approximately 60 % of all WEEE samples therein. These variations may in part be due to the presence of NBFRs alongside TBBP-A, HBCDD and PBDEs, reflecting the

XRF instrument's inability to specify the precise chemical form of bromine present in samples.

3.2.2 – Furniture and Vehicle Foam

The XRF and MS derived concentrations of Br in 43 PUF samples are compared (*Figure 3*) showing a slope of 1.70 and a R^2 value of 0.98. The high regression coefficient for these samples is likely the result of interferences with primary and secondary x-rays in the high thickness and low density of the PUF samples examined. Internal XRF approximations of the sample's density using Compton scattering can be heavily influenced due to the presence of air pockets in the samples, leading to a significant bias in the accurate quantification of elemental bromine (and other elements) (Zawisza, 2012). However, assuming these biases are relatively consistent throughout different PUF samples, measured results can be subsequently multiplied by a correction factor derived from the inverted slope of linear regression to correct this bias.

Although this correction factor ($\mu_{\text{puf}} = 1.70^{-1} = 0.59$) can improve the accuracy of the XRF-measurements, its precision in the analysis of PUF samples remains unreliable, with relative standard deviation (RSD) for individual measurements ranging from 1 % to 172 % ($\text{RSD}_{\text{avg}} = 39 \%$). In addition, repeated XRF analyses of PUF samples on a dedicated test stand in a controlled laboratory setting showed high variability in Br content depending on the orientation of the sample and the surface facing the analyser window. It was observed upon repeated laboratory measurements of eight furniture foam samples whose XRF results deviated by >250 % from the corresponding MS-concentrations, that five of the samples had shown substantial differences (z-test, $p < 0.001$) in the detected concentration of bromine on surfaces which were cut away from the body of the PUF item compared to the surface adjacent to the upholstery (*S1 (a), S4*). This – akin to previous observations of BFR migration

from fabric to dust via direct contact (Rauert et al., 2016) is consistent with migration of BFRs from overlying upholstery fabric into underlying PUF, resulting in higher concentrations of BFRs in PUF near contact surfaces and spatially declining concentrations deeper within the material.

3.2.3 – Furniture and Vehicle Upholstery

For the regression of the 66 upholstery samples included a slope of 1.38 and a R^2 of 0.86 were determined (*S5 (a)*), indicating a strong correlation between the analytical techniques. Similar to the PUF samples, the upholstery samples also appear to require a correction factor ($\mu_{\text{upholstery}} = 1.38^{-1} = 0.72$) in order to account for the relatively low density of the material and the resultant matrix effects. However, a Bland-Altman plot similar to *Figure 2 (a)* demonstrated the XRF's overestimation of bromine concentrations by up to 180 % for concentrations exceeding 100 mg kg^{-1} and several thousand percent for lower concentrations. This phenomenon may simply be more obscured at larger concentrations due to the magnitude of concentrations involved and also possibly due to a “screening-effect” within the matrix of the material during XRF analysis, whereby multiple bromine atoms are in a linear formation with respect to the analyser resulting in only the first and none of the subsequent bromine atoms being detected (Zawisza, 2012).

The relative homogeneity of repeated XRF measurements and the high discrepancies between Br concentrations obtained via the two measurement techniques revealed in the Bland-Altman plot (*S1 (b)*), are – as for PUF materials – likely attributable to the presence of BFRs not measured in this study or, in the case of some ELV samples containing green upholstery, the use of green pigment containing bromine. In similar fashion to WEEE samples (*Section 3.2.1*), only 25 % of samples yielded Br concentrations derived by XRF that agreed within ± 25 % of those obtained via MS (following application of the correction factor). However,

given the high treatment concentrations with HBCDD and Deca-BDE, the XRF could still be successfully applied to the screening of upholstery for excess POP-BFRs as false-positives (instances where XRF analysis indicates exceedance of an LPCL where none actually occurred) at such elevated bromine concentrations were rare in this study.

3.2.4 –Insulation Foams - Expanded Polystyrene (EPS)

Of the 47 original EPS samples, 17 were excluded from the analysis due to determination of Br concentrations below LOD_X . Br concentrations obtained for the remaining samples via XRF and MS underwent regression analysis (*Figure 4*) showing a linear slope of 1.20 and R^2 of 0.98. The XRF measurements again appear to require a calibration factor in order to correct the regression for offsets caused by matrix effects. Implementing this, XRF measurements of 16 out of 30 samples correlate to within 25 % of MS results with 12 of these 16 (for which Br $>1000\text{ mg kg}^{-1}$) agreeing to within 10 % of MS-determined bromine content.

Despite this favourable agreement for samples containing higher Br concentrations (i.e. $>1000\text{ mg kg}^{-1}$) analysis of the data using a Bland-Altman plot (*SI (c)*) reveal potentially significant outliers in this sample group most notably in the 0-10 mg kg^{-1} Br concentration range (z-test, $p < 0.05$), as determined by MS analysis, despite exclusion of samples $<LOD_X$. Additionally, the relative standard deviations (RSDs) of the triplicate XRF measurements indicate that the samples showing poor agreement between XRF and MS have large RSDs ($>25\%$) between the individual XRF measurements, the largest RSDs (173 % each) being attributed to the significant outliers highlighted in *SI (c)*. Selection criteria for more accurate categorisation of Br concentrations can potentially be established from these observations; specifically, omission of samples with 0-10 mg kg^{-1} Br-content (from MS analysis) and those

with RSDs over 25 % (from triplicate XRF analysis, results in over 80 % of samples being categorised as accurate to within 10 % of the true HBCDD concentration.

One noteworthy EPS sample showed a much larger discrepancy between XRF-determined bromine (average bromine = 3354 mg kg⁻¹; RSD = 12 %) and LC-MS/MS (total bromine = 1030 mg kg⁻¹) analyses. Repeat XRF measurements of the same sample in-lab yielded an average for four measurements of 4275 mg kg⁻¹ bromine with a RSD of 19 % – the higher RSD being attributable to the small sample size relative to the XRF measurement window, such that primary x-rays are not interacting with the target sample. Such a variation between XRF-determined- and LC-MS/MS-determined bromine did not occur in any other samples within this group, potentially indicating another bromine-based compound in this particular sample, such as tribromoallylether or PolyFR (Schlummer et al., 2015, IPCS, 1997).

3.2.5 –Insulation Foams - Extruded Polystyrene (XPS)

The linear regression for the 20 XPS samples for which XRF- and MS-derived Br measurements were compared (*S5 (b)*) shows a linear slope of 1.93 with a R² of 0.97. This sample group shows the largest deviation from a unity regression. Following correction, a Bland-Altman plot (*SI (d)*) shows an even distribution for samples for containing >200 mg kg⁻¹ bromine. However, the variation between the two Br metrics at concentrations up to 200 mg kg⁻¹ remains high (±100 %).

This sampling, however, contained only a few with excessive concentrations of BFRs, and too few overall for a more definitive linear regression. Relatively few samples have been treated with BFRs and generally at much lower concentrations and other waste categories based on this sampling. However, a more statistically significant sample size may reveal as yet unseen nuances to this plastic.

4. Discussion

4.1 Utility of XRF Instrumentation as a Pass/Fail Screening Tool for LPCL Compliance

In the context of portable XRF's potential use as a tool for testing compliance with POP-BFR LPCL values, the incidence of "false positives" and "false negatives" is crucial. A "false positive" is defined here as a specific source misclassification scenario, i.e. a situation where the XRF measurement of Br indicates the LPCL for a POP-BFR to be exceeded, but the POP-BFR concentration is below the LPCL. By comparison, a "false negative" occurs where the POP-BFR concentration is above the LPCL, but this is not indicated by the XRF measurement of Br (*Section 3*). For the purposes of discussion here, we have assumed a conservative Br LPCL value based on the Br detected being due to penta-BDE. Thus, any sample exceeding 710 mg Br/kg is assumed here to exceed the POP-BFR LPCL of 1,000 mg POP-BFR/kg (including 1000 mg kg⁻¹ limit for Deca-BDE established by REACH).

Of the 555 items we tested, there were 34 false positives and no false negatives when the current LPCLs for POP-BFRs are considered: 26 occurred in WEEE items (1 large household appliance, 12 display items, 6 small domestic appliances, and 7 IT items); the remainder, in 2 vehicle fabric samples, 1 vehicle foam sample, 1 carpet sample, 1 mattress foam sample, 1 furniture upholstery sample, and 2 furniture foam samples. These resulted from concentrations >1,000 mg kg⁻¹ of either TBBP-A alone (n=15), as yet unidentified bromine-containing compounds (n=11), and in 8 instances enhancement of measured BFR concentrations. However, 5 of the 11 samples with unidentified compounds are attributable to false-positives due to background interference (*Section 3.2.1*) which therefore reduces the number of false-positives to 29 of 555. Translating these incidences into percentages, our data show that use of portable XRF to monitor compliance with current LPCLs for PBDEs and HBCDD would mean that 5.2 % of articles from the waste categories studied would be

incorrectly identified as requiring special treatment. This compares to 47 (8.5 %) of articles identified as genuinely exceeding current LPCLs and REACH limits.

The implications of such false positives are essentially that a small additional percentage of articles will not be available for recycling and that there will be an additional unnecessary economic cost incurred when such articles are subjected to special treatment. Balanced against these issues, it may be argued that as the cause of the false positives are likely to be either known or unidentified BFRs not targeted in our study, which may themselves become subject to future legislative restriction; false positives can potentially be viewed as an acceptable limitation of the use of XRF as a screening tool for LPCL compliance. By comparison, false negatives would exert a more detrimental impact as they would allow regulated POP-BFRs to remain in circulation. However, the absence of false negatives in our study, suggests that use of hand-held XRF will only very rarely – if ever - fail to identify articles that exceed LPCL values.

Our data on false positives indicate that portable XRF could be a viable tool for testing compliance with LPCLs for EPS/XPS, as well as ELV waste and waste soft furnishings, while further underlining the potential issues with the use of hand-held XRF to test for LPCL compliance in WEEE due to the more frequent presence of TBBP-A and other as yet unidentified compounds in such items.

4.2 Accuracy and Precision of XRF-Determined Bromine as a Surrogate for POP-BFRs

Upon comparing the results of total Br from portable XRF analysis with compound-specific mass spectrometry, the overall *accuracy* of XRF strongly depends on the type of polymer under investigation. Though the regression of all sample-groups appears to follow a generally linear correlation between XRF and MS results, the deviation of the slopes from unity in most

of the plastic types indicates that matrix effects occur prominently in low-density materials. Br concentrations obtained from XRF measurements were adjusted based on subsequent mass spectrometric analyses of the same samples thus allowing for a correction factor to be inferred (*Section 3.2*). However, for use of this instrument as a standalone analyser for accurately quantifying total bromine concentrations in the range of materials studied here, suitable calibration standards unique to each type of polymer (ABS, HIPS, PUF, etc.) would initially be required to ensure reliable compensation for matrix effects. Application of correction factors to XRF measurements discerned following MS analysis was successful in correcting the overall accuracy of the instrument for all measured concentrations, with little effect on the deviations for individual measurements.

These corrections had little effect on the deviations for individual measurements however; therefore, the estimated *precision* of the instrument still requires further refinement. In all but one of the sample groups studied, the deviation of XRF analysis from the MS-determined bromine content of the samples significantly exceeded a 95 % confidence interval. These variations may be due to the elemental and chemical composition of individual samples interfering with XRF analyses in ways unique to each sample. Additionally, as shown by the occurrence of background interference in WEEE samples (*S4*), the penetration-depth of x-rays is not finite as they permeate through thin plastic items to the substrate material thereby skewing estimations of the sample's density by the instrument (*Section 3.2.1*).

As shown earlier, further uncertainties may be attributable in some cases to the presence in samples of BFRs not targeted herein. The presence of these other BFRs (or other bromine-based compounds) also acts as an obstacle to the more effective use of XRF an accurate metric of POP-BFR concentrations (*Figure 1*). This is mainly due to the inherent lack of selectivity of XRF, which renders it incapable of distinguishing between POP-BFRs and other bromine-containing compounds contributing to the total Br concentration. The precise

detection of POP-BFRs by XRF will be exacerbated further by the presence of multiple BFRs within the same sample-groups by the further-use of nBFRs.

Based on the present study, EPS and XPS constitute the groups which could most reliably utilise XRF-quantified bromine as a surrogate for POP-BFRs *in situ* at recycling sites, showing the highest number of samples with the lowest deviations from true bromine content. Both groups would require specific calibration to compensate for matrix effects and improve the overall accuracy of analyses. In its current state, XRF-determined bromine measurements are unsuitable as a surrogate for POP-BFR determination in the remaining sample groups investigated herein. Refinements to measurement protocols (*e.g.* material separation to avoid background interference in WEEE) and the inclusion of reference standards specific to each type of plastic could improve the accuracy of the XRF instrument. However, specific matrix effects inherent in low density materials, varying chemical composition of the analyte materials, and the presence of non-POP-BFRs, and the lack of specificity of XRF in determining bromine species constitute substantial obstacles to the standalone use of XRF for the accurate quantification of POP-BFRs in plastic media.

5. Conclusions

Our study clearly shows that portable XRF cannot be used to accurately determine absolute concentrations of POP-BFRs. However, its use as a screening tool for LPCL compliance appears to be viable, provided sufficient prior knowledge of typical BFR-treatment in different plastics is available and the number of samples misclassified as exceeding LPCLs is deemed acceptable or can be reduced. Of particular note is the applicability of XRF for screening EPS and XPS materials above the proposed LPCL threshold (710 mg kg⁻¹) due to the observed high precision shown for quantifying POP-BFRs in these materials. However,

the results obtained from the standalone use of XRF measurements as a surrogate for POP-BFR determination in the other plastic types investigated agree with conclusions previously reached by Gallen et al. (2014) and Petreas et al. (2016), namely that significant inconsistencies between measurement techniques result in XRF alone being insufficient to precisely determine BFRs, furthermore requiring MS to identify concentrations of specific BFRs. Application of reference standards such as those utilized by Guzzonato et al. (2016) can further enhance the accuracy of XRF as a surrogate measure of BFR concentrations. Restricting screening solely to non-WEEE items further reduces the frequency of false positives to 2.5 %. To ensure that waste plastics are being recycled effectively and safely, the validity of XRF screening for compliance with LPCLs for POP-BFRs should remain an ongoing field of investigation, in particular with respect to matrix effects and the need for calibration standards, and the expected further use of NBFRs in recyclable plastics.

In summary, our study shows that while portable XRF may be used as a reliable (though not infallible) “pass-fail” indicator of compliance with LPCLs for POP-BFRs. We also show that refinements to measurement protocols (*e.g.* material separation to avoid background interference in WEEE) and the inclusion of reference standards specific to each type of plastic could potentially reduce the incidence of “false positives” resulting from use of portable XRF, thereby diminishing the number of waste items incorrectly identified as requiring special treatment.

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549 **References**

- 550 ABDALLAH, M. A.-E., DRAGE, D. S., SHARKEY, M., BERRESHEIM, H. & HARRAD, S. 2017. A rapid
 551 method for the determination of brominated flame retardant concentrations in plastics and
 552 textiles entering the waste stream. *Journal of Separation Science*, 40, 3873-3881.
- 553 ABDALLAH, M. A.-E., IBARRA, C., NEELS, H., HARRAD, S. & COVACI, A. 2008. Comparative evaluation
 554 of liquid chromatography–mass spectrometry versus gas chromatography–mass
 555 spectrometry for the determination of hexabromocyclododecanes and their degradation
 556 products in indoor dust. *Journal of Chromatography A*, 1190, 333-341.
- 557 AL-OMRAN, L. & HARRAD, S. Distribution patterns of legacy and "novel" brominated flame
 558 retardants in different particle size fractions of indoor dust in Birmingham, UK. 10th
 559 Network Conference on Persistent Organic Pollutants (POPs): Environmental Organic
 560 Pollutants, Metabolites and Transformation Products, 13th April 2016 2016 Winterbourne
 561 House and Garden, University of Birmingham. 10th Network Conference on POPs.
- 562 ALDRIAN, A., LEDERSTEGER, A. & POMBERGER, R. 2015. Monitoring of WEEE plastics in regards to
 563 brominated flame retardants using handheld XRF. *Waste Manag*, 36, 297-304.
- 564 DRAGE, D., SHARKEY, M., ABDALLAH, M. A., BERRESHEIM, H. & HARRAD, S. 2018. Brominated flame
 565 retardants in Irish waste polymers: Concentrations, legislative compliance, and treatment
 566 options. *Science of The Total Environment*, 625, 1535-1543.
- 567 EC 2004. EC regulation no. 850/2004 of the European Parliament and of the Council of 29 April 2004
 568 on persistent organic pollutants and amending Directive 79/117/EEC. *OJL*, 158, 7.
- 569 EC 2010. Commission regulation no 756/2010 of 24 August 2010 amending regulation (EC) No
 570 850/2004 of the European Parliament and of the Council on persistent organic pollutants as
 571 regards Annexes IV and V. 223, 20.
- 572 EC 2011. Final Report: Study on waste related issues of newly listed POPs and candidate POPs. *In*:
 573 (ESWI), E. T. T. S. W. I. (ed.). Munich: European Commission.
- 574 EC 2016. Commission regulation (EU) 2016/460 of 30 March 2016 amending Annexes IV and V to
 575 regulation No 850/2004 of the European Parliament and of the Council on persistent organic
 576 pollutants. *Off. J. Eur. Commun*.
- 577 EPA. 2016. *WEEE Statistics for Ireland* [Online]. Environmental Protection Agency of Ireland.
 578 Available:
 579 [http://www.epa.ie/pubs/reports/waste/stats/weeedata2013/EPA_WEEE_2013_data_releas](http://www.epa.ie/pubs/reports/waste/stats/weeedata2013/EPA_WEEE_2013_data_release_web.pdf)
 580 [e_web.pdf](http://www.epa.ie/pubs/reports/waste/stats/weeedata2013/EPA_WEEE_2013_data_release_web.pdf) [Accessed 07-03-18 2018].
- 581 EU 2017a. COMMISSION REGULATION (EU) 2017/227 of 9 February 2017 amending Annex XVII to
 582 Regulation (EC) No 1907/2006 of the European Parliament and of the Council concerning the
 583 Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH) as regards
 584 bis(pentabromophenyl)ether *Official J Eur Union*, 35, 6-9.
- 585 EU 2017b. COUNCIL REGULATION (EU) 2017/997 of 8 June 2017 amending Annex III to Directive
 586 2008/98/EC of the European Parliament and of the Council as regards the hazardous
 587 property HP 14 'Ecotoxic'. *Official Journal of the European Union*, 150, 1-4.
- 588 GALLEN, C., BANKS, A., BRANDSMA, S., BADUEL, C., THAI, P., EAGLESHAM, G., HEFFERNAN, A.,
 589 LEONARDS, P., BAINTON, P. & MUELLER, J. F. 2014. Towards development of a rapid and
 590 effective non-destructive testing strategy to identify brominated flame retardants in the
 591 plastics of consumer products. *Sci Total Environ*, 491-492, 255-65.
- 592 GROSSE, Y., LOOMIS, D., GUYTON, K. Z., EL GHISSASSI, F., BOUVARD, V., BENBRAHIM-TALLAA, L.,
 593 MATTOCK, H. & STRAIF, K. 2016. Carcinogenicity of some industrial chemicals. *The Lancet*
 594 *Oncology*, 17, 419-420.

- GUZZONATO, A., PUYPE, F. & HARRAD, S. J. 2016. Improving the accuracy of hand-held X-ray fluorescence spectrometers as a tool for monitoring brominated flame retardants in waste polymers. *Chemosphere*, 159, 89-95.
- IPCS. 1997. *Flame retardants (EHC 192, 1997)* [Online]. World Health Organisation. Available: <http://www.inchem.org/documents/ehc/ehc/ehc192.htm> [Accessed March 14 2016].
- MALKOSKE, T., TANG, Y., XU, W., YU, S. & WANG, H. 2016. A review of the environmental distribution, fate, and control of tetrabromobisphenol A released from sources. *Science of The Total Environment*, 569-570, 1608-1617.
- MARVIN, C. H., TOMY, G. T., ARMITAGE, J. M., ARNOT, J. A., MCCARTY, L., COVACI, A. & PALACE, V. 2011. Hexabromocyclododecane: Current Understanding of Chemistry, Environmental Fate and Toxicology and Implications for Global Management. *Environmental Science & Technology*, 45, 8613-8623.
- MORF, L., TAVERNA, R., DAXBECK, Z. H. & SMUTNY, R. 2003. Selected polybrominated flame retardants PBDEs and TBBPA: Substance flow analysis. *Environmental Series No 338: Environmentally Hazardous Substances*.
- PETREAS, M., GILL, R., TAKAKU-PUGH, S., LYTLE, E., PARRY, E., WANG, M., QUINN, J. & PARK, J.-S. 2016. Rapid methodology to screen flame retardants in upholstered furniture for compliance with new California labeling law (SB 1019). *Chemosphere*, 152, 353-359.
- PETTY, S., LINDEMAN, A. E., BLUM, A., BELLUR, S., DIAMOND, M. L., LUCAS, D., KOSHLAND, C. P. & WEBER, R. MANAGEMENT OF HALOGENATED FLAME RETARDED WASTES IN THE UNITED STATES –THE NEED FOR A CIRCULAR ECONOMY APPROACH. 36th International Symposium on Halogenated Organic Pollutants, 28th August 2016 2016 Palazzo Dei Congressi, Firenze. 36th International Symposium on Halogenated Organic Pollutants.
- RAUERT, C., HARRAD, S., SUZUKI, G., TAKIGAMI, H., UCHIDA, N. & TAKATA, K. 2014. Test chamber and forensic microscopy investigation of the transfer of brominated flame retardants into indoor dust via abrasion of source materials. *Sci Total Environ*, 493, 639-48.
- RAUERT, C., KURIBARA, I., KATAOKA, T., WADA, T., KAJIWARA, N., SUZUKI, G., TAKIGAMI, H. & HARRAD, S. 2016. Direct contact between dust and HBCD-treated fabrics is an important pathway of source-to-dust transfer. *Science of The Total Environment*, 545-546, 77-83.
- SCHLUMMER, M., VOGELSANG, J., FIEDLER, D., GRUBER, L. & WOLZ, G. 2015. Rapid identification of polystyrene foam wastes containing hexabromocyclododecane or its alternative polymeric brominated flame retardant by X-ray fluorescence spectroscopy. *Waste Manag Res*, 33, 662-70.
- SINDIKU, O., BABAYEMI, J., OSIBANJO, O., SCHLUMMER, M., SCHLUEP, M., WATSON, A. & WEBER, R. 2015. Polybrominated diphenyl ethers listed as Stockholm Convention POPs, other brominated flame retardants and heavy metals in e-waste polymers in Nigeria. *Environmental Science and Pollution Research*, 22, 14489-14501.
- UNEP 2009. Stockholm Convention on Persistent Organic Pollutants (as amended 2009). In: UNEP (ed.). Stockholm, Sweden: United Nations Environment Programme.
- UNEP 2010. Technical review of the implications of recycling commercial pentabromodiphenyl ether and commercial octabromodiphenyl ether. In: COMMITTEE, P. O. P. R. (ed.). Geneva: United Nations Environmental Programme.
- UNEP 2013. An amendment to Annex A adopted by the Conference of the Parties to the Stockholm Convention on Persistent Organic Pollutants at its sixth meeting (Decision SC-6/13). In: UNEP (ed.). Stockholm, Sweden: United Nations Environment Programme.
- UNEP 2017a. COP-8/32: Report on the Conference of Parties to the Stockholm Convention on persistent Organic Pollutants on the works of its eighth meeting. In: UNEP (ed.). Geneva, Switzerland: United Nations Environment Programme.
- UNEP 2017b. Guidance for the inventory of Hexabromocyclododecane (HBCD). In: PROGRAMME, U. N. E. (ed.) SC-7/10. Switzerland: Secretariat of the Stockholm Convention.

- 645 WEIL, E. D. & LEVCHIK, S. V. 2009. Flame Retardants in Commercial Use of Development for Textiles.
646 *Journal of Fire Sciences*, 26, 243-281.
647 ZAWISZA, R. S. B. 2012. Quantification in X-Ray Fluorescence Spectrometry. *In*: SHARMA, S. K. (ed.)
648 *X-Ray Spectroscopy*. InTech.

649

TABLES

Table 1 – Statistical summary of total XRF-Br and MS-BFR concentrations categorized by Waste Type.

Waste Type	Sample Group	Total No. of Samples (N)	XRF-Br Range (mg kg ⁻¹)	XRF-Br Median (mg kg ⁻¹)	MS-ΣBFRs Range (mg kg ⁻¹)	MS-ΣBFRs Median (mg kg ⁻¹)	Number of Samples for Regression
Waste Electrical and Electronic Equipment (WEEE)	IT & Telecoms *	78	0 – 110,000	18	0 – 110,000	0.5	36
	Small Domestic Appliances *	26	0 – 1,900	1	0 – 10,000	0.1	7
	Display *	43	0 – 150,000	320	0 – 270,000	58	27
	Large Household Appliances	57	0 – 2,100	0	0 – 2,000	0.04	0
	Fridge/Freezer	30	0 – 14	0	0 – 3.6	0	0
Expanded Polyurethane Foams	Furniture Foam *	20	0 – 12,000	110	0 – 8,500	100	17
	Mattress Foam	17	0 – 880	59	0 – 870	8.4	0
	ELV Foam *	38	0 – 780	14	0 – 740	1.6	26
Fabrics & Upholstery	Furniture Upholstery *	22	0 – 87,000	320	0 – 73,000	112	17
	Mattress Upholstery	17	0 – 240	10	0 – 58	8.7	0
	ELV Upholstery *	50	0 – 35,000	72	0 – 31,000	17	49
Construction & Demolition	C&D EPS *	40	9,200	45	0 – 10,000	83	27
	C&D XPS *	20	160	23	0 – 94	20	16
Packaging	Pack EPS *	7	0 – 5,600	18	0 – 5,900	1.1	3
	Pack XPS *	14	0 – 1,300	2	0 – 370	0.2	4
Other Textiles & Plastics	ELV (other)**	30	0 – 28,000	12	0 – 23,000	3.8	0
	Curtain	15	0 – 88	3	0 – 58	0	0
	Carpet	31	0 – 9,600	8	0 – 7,000	0.1	0

* Sample-groups included for regression analysis (see Section 3.2).

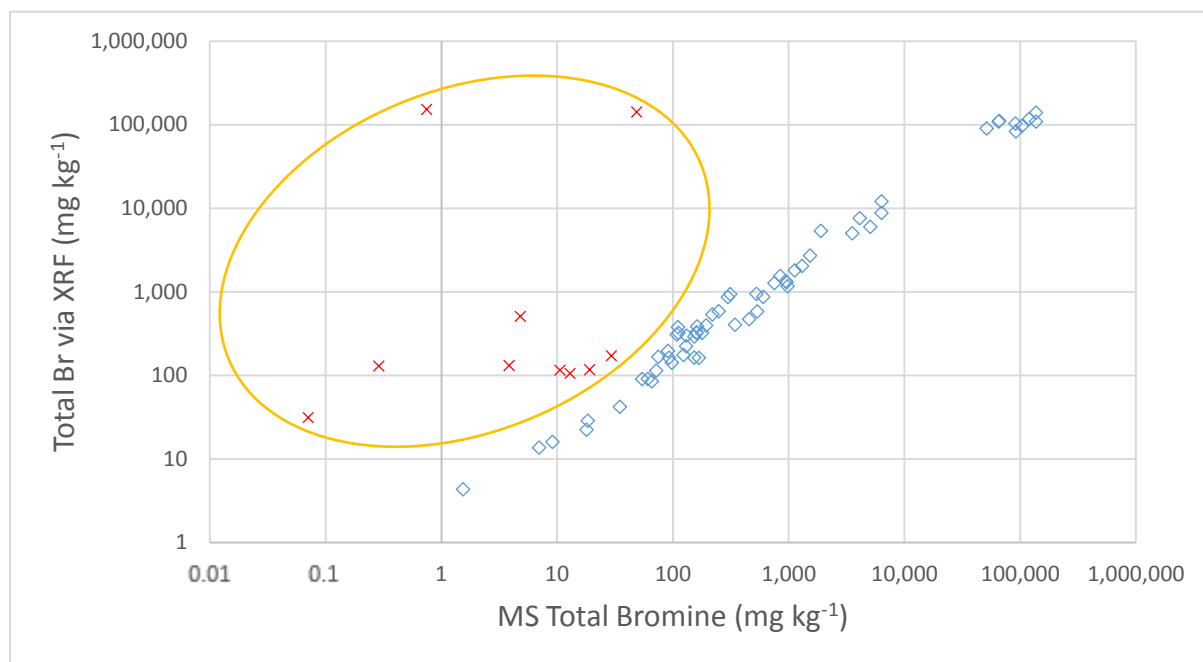
** Sample-group consists of plastics from roof trim, floor mats, under seat EPS padding, etc. thus making it unsuitable for regression of similar materials.

Figure Captions

- Figure 1* *Regression between total Br concentrations (mg kg^{-1}) measured by XRF and GC/MS / LC-MS/MS for 70 WEEE samples (slope $m = 0.98$, $R = 0.78$ $R^2 = 0.61$). Data represented by “x” symbols (inset outlined portion) show samples suspected of having NBFRs or other bromine-containing compounds. Omitting those data yields $m = 0.91$, $R = 0.96$, $R^2 = 0.93$.*
- Figure 2 (a)* *Bland-Altman plot for WEEE samples showing the deviation of XRF-determined Br from MS-quantified Br (%), with the latter assumed to represent true Br values (mg kg^{-1}).*
- Figure 2 (b)* *Exploded view of data from Figure 2 (a) highlighting samples in lower deviation bracket and omitting those outliers attributed to NBFR presence as outlined in Figure 1.*
- Figure 3* *Regression between total Br concentrations (mg kg^{-1}) measure by XRF and GC/MS / LC-MS/MS for 43 PUF samples (slope $m = 1.70$, $R = 0.99$, $R^2 = 0.98$).*
- Figure 4* *Regression between total Br concentrations (mg kg^{-1}) measure by XRF and GC/MS / LC-MS/MS for 30 EPS samples ($m = 1.20$, $R = 0.99$, $R^2 = 0.98$).*

19 **FIGURES**

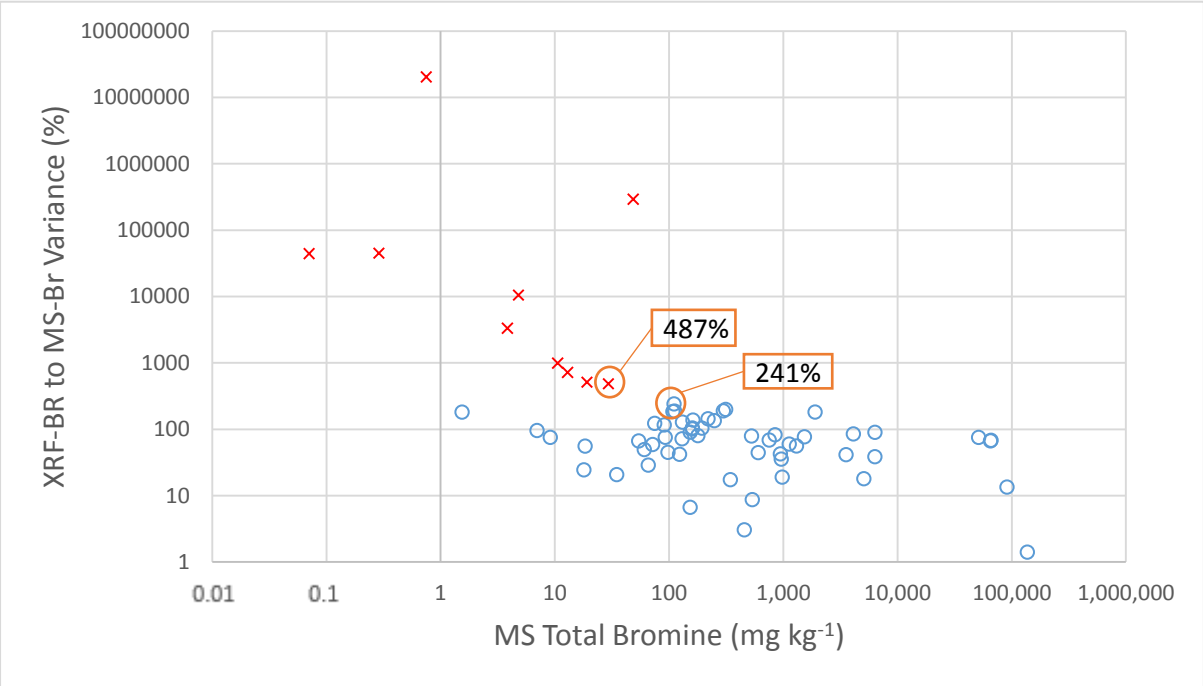
20 *Figure 1*



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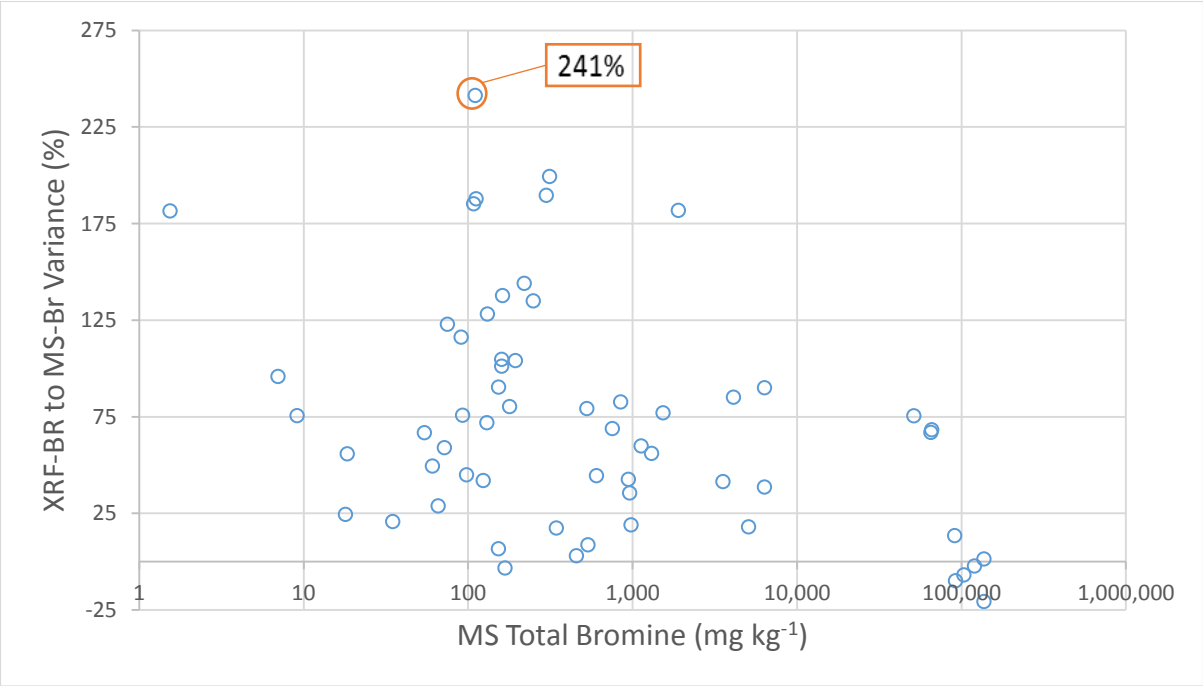
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23 *Figure 2 (a)*



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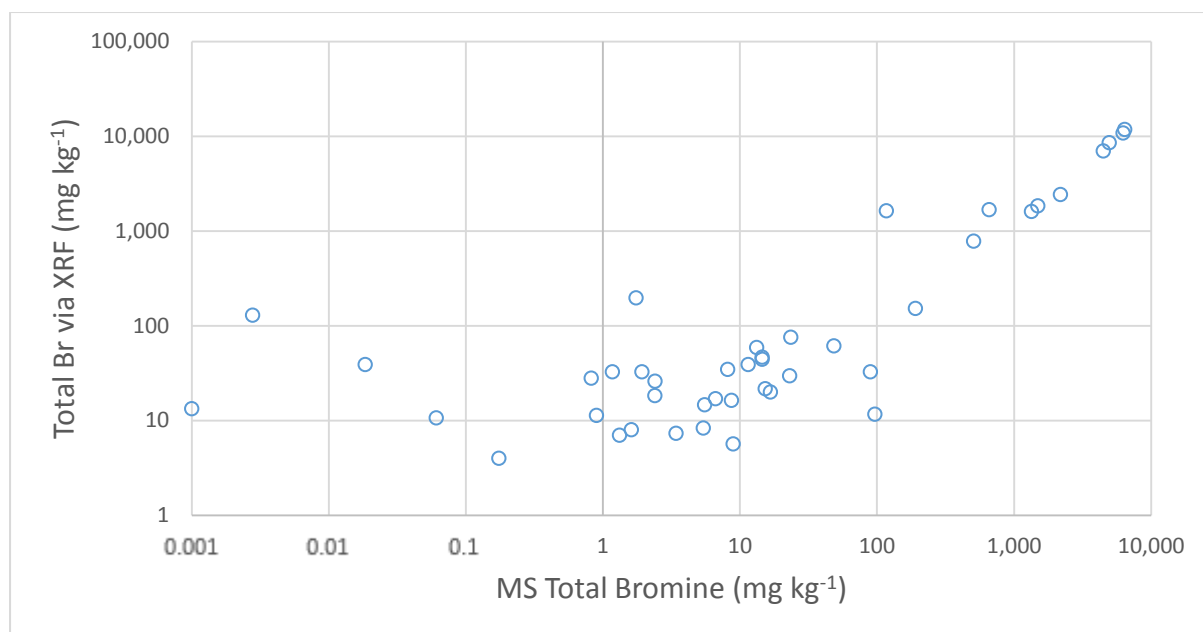
25 *Figure 2 (b)*



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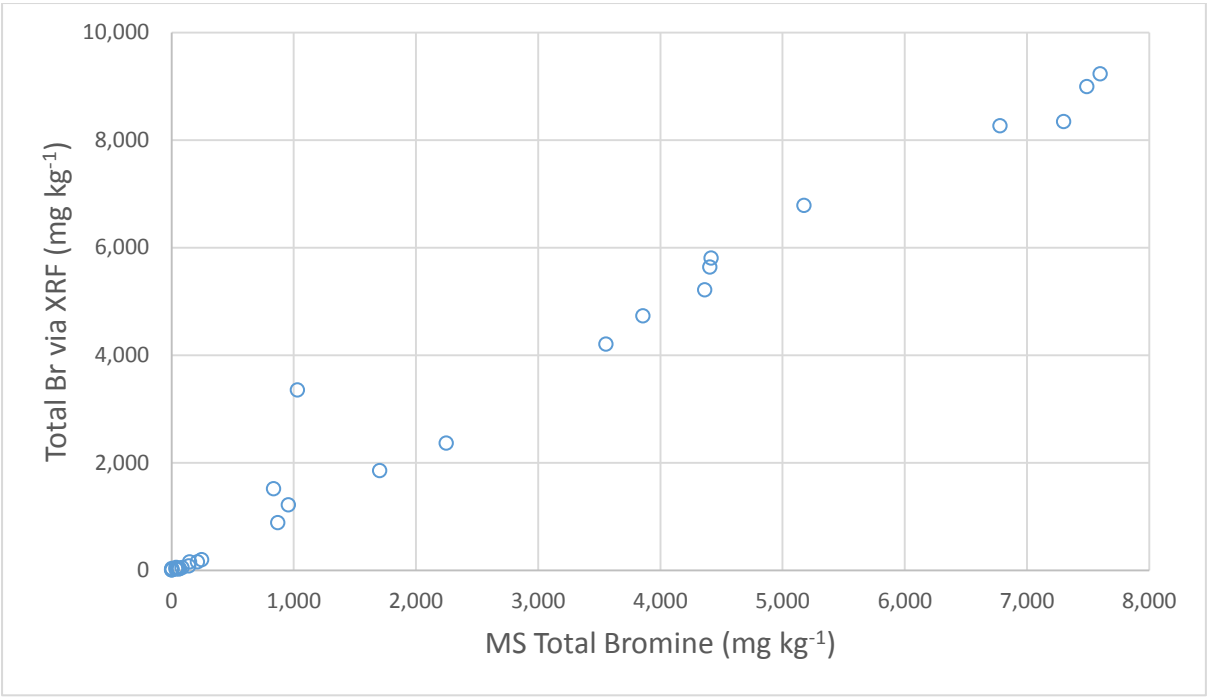


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33 *Figure 4*



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